Basic Quantum Mechanics

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Old quantum theory



Origin of the Quantum Theory

In 1900, the German physicist Max Plank discovered an empirical relation that agreed with the entire continuous spectrum emitted by a black-body radiator.

A black-body is defined as the body which absorbs all incident electromagnetic radiation. Max Plank then worked to find a physical explanation for his formula and succeeded in doing this after several weeks work.

His results were the origin of the quantum theory. The first quarter of the present century saw the subsequent development of the (*Old Quantum Theory*) which was to be superceded in 1925 by the (*wave mechanics*).

Plank assumed that a black-body is composed of oscillators in equilibrium with the radiation field and his basic assumption was that the material oscillators can only have discrete energy levels rather than a continuous range of energies.

In particular Planck assumed that an oscillator with frequency ν can only take the values:

$$E_n = nh\nu \quad , n = 0,1,2\cdots$$

Where h is a universal constant, later to be known as the Plank constant.

Planck chose the value

$$h = 6.55 \times 10^{-34} \text{ joulesec}$$

To agree with the experimental results but the value accepted today is

$$h = 6.62 \times 10^{-34} \text{ joulesec}$$

Niels Bohr

In 1913 the Danish physicist Niels Bohr made two basic

Postulates:

i. He assumed that the electron is a particle that can revolve about the nucleus only in certain allowed orbits which may be Circular or elliptical. Each orbit represents a stationary energy state in which electromagnetic radiation is not emitted, in conflict with the predictions of classical theory. The allowed orbits or states are those in which the angular momentum of the electron about the nucleus is an integer multiple of

$$\hbar = h/2\pi$$

$$m v r = n\hbar$$

ii. Emission or absorption of radiation occurs when the electron makes a quantum jump from one stationary state to another when the atom makes a transition from a higher energy state E_i to a lower energy state E_f.

Bohr suggested, (*following Planck*) that the energy difference is radiated as a photon of frequency ν with :

$$E_i - E_f = h\nu \quad [1]$$

An outline of the Bohr Theory is giving below.

Bohr used classical methods to calculate the energy of his allowed stationary states.

The force of attraction between the hydrogen nucleus and the electron is:

$$F = \frac{ze^2}{r^2} \quad [2]$$

Where r is the distance of the electron from the nucleus.

The simplest case is that of a circle and the inward force is:

$$F = m\frac{v^2}{r} \text{.......................................} [3]$$

Where m is the electron mass and v is the speed .
From equation (2) , (3) , the kinetic energy is seen to be :

$$T = \frac{1}{2}mv^2 = \frac{ze^2}{2r} \text{...........................} [4]$$

The potential energy of the electron is given by:

$$V = \frac{-ze^2}{r}$$

And so the total energy of the electron in a circular orbit of radius r is:

$$E = T + V = \frac{-ze^2}{2r} \text{.........................} [5]$$

From Bohr's first postulate the radii of the allowed orbits are given by

$$mvr = n\hbar \quad ,n = 1,2,3,\cdots \text{................} [6]$$

From (4), (6) it is possible to give:

$$\because m^2v^2 = \frac{ze^2}{2r}\cdot 2m = \frac{n^2\hbar^2}{r^2}$$

$$\therefore mze^2 = \frac{n^2\hbar^2}{r}$$

$$r = \frac{n^2\hbar^2}{mze^2} \quad \text{.....................................[7]}$$

And the energies of the allowed states are:

$$E_n = -\frac{mz^2e^4}{2\hbar^2n^2}, n = 1,2,3,\cdots \quad \text{.......[8]}$$

When an electron jumps from the n_i orbit to the n_f orbit the frequency of the radiation emitted is given by:

$$\nu = \frac{E_i - E_f}{h}$$

$$i.e \quad \nu = \frac{2\pi^2mz^2e^4}{h^3}\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right] \quad \text{....[9]}$$

The wave number of the radiation is given by:

$$\frac{k}{2\pi} = \frac{1}{\lambda} = \frac{\nu}{c} \quad \text{and also}$$

$$\frac{k}{2\pi} = \frac{2\pi^2mz^2e^4}{h^3c}\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right]$$

$$\frac{k}{2\pi} = R\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right] \quad \text{......................[10]}$$

Where the constant R is given by:

$$R = \frac{2\pi^2mz^2e^4}{h^3c}$$

Wilson and Sommerfeld

Bohr's theory dealt only with circular orbits.

A. Sommerfeld (1916) [*and also Wilson (1915)*], generalized the Bohr theory to include elliptic orbits.

He said that the allowed states of a periodic system are determined by the quantum conditions

$$\oint P_i \, dq_i = n_i h \quad , n_i \text{ integer}$$

Where P_i the momentum conjugates to the coordinate q_i and the integration is over a complete period of the motion. (*simple harmonic oscillator*).

When the Wilson – Sommerfeld rule is applied to the linear harmonic oscillator, the energy levels used by Planck are obtained.

Consider a particle of mass m oscillating about the origin in the x – direction. If the coordinate of which is given by:

$$x = a \sin \omega t \quad \text{..[1]}$$

And the period τ and the energy E

$$\therefore J_x = \oint P_x \, dx = n h$$

$$J_x = \oint m a^2 \omega^2 \cos^2 \omega t \, dt$$

$$let \; \theta = \omega t \Rightarrow d\theta = \omega \, dt$$

$$J_x = \int_0^{2\pi} \frac{m a^2 \omega^2}{\omega} \cos^2 \theta \, d\theta$$

$$note\ that\ \cos^2\theta = \frac{1}{2}(1+\cos 2\theta)$$

$$J_x = \frac{1}{2}\frac{m\,a^2\omega^2}{\omega}(2\pi)$$

$$= \frac{1}{2}m\,a^2\omega^2\tau$$

$$\therefore J_x = E\tau \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots[2]$$

$$\therefore E\tau = n\,h \qquad n = 1,2,3,\cdots$$

$$\therefore E_n = n\,h\,\nu \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots[3]$$

This is the Planck's quantum condition.

If we apply the above quantization rule to the circular orbits the result is the same as the first Bohr assumption

$$\oint P_\theta\, d\theta = \oint m\,v\,r\,d\theta$$

$$\oint P_\theta\, d\theta = 2\pi m\,v\,r = n\,h \quad \ldots\ldots\ldots\ldots[4]$$

Therefore $\quad 2\pi m\,v\,r = n_\theta h$

Or $\quad m\,v\,r = n_\theta\hbar\,. \quad \ldots\ldots\ldots\ldots[5]$

Consequently, these two results can be extended to a general applicability of the Wilson–Sommerfeld quantization rule.

Elliptic electron orbit

Consider an electron revolving about the hydrogen nucleus in a plane elliptic orbit, with the nucleus at one focus.

The single Bohr condition is replaced by the two conditions:

$$\oint P_r\, dr = n_r h \text{ ....} [1]$$

$$\oint P_\varphi\, d\varphi = n_\varphi h \text{ ....} [2]$$

Where n_r, n_φ are both integers. The momentum P_φ is simply the angular momentum and from Kepler's law is a constant.

$$\therefore P_\varphi 2\pi = n_\varphi h \qquad or \quad P_\varphi = n_\varphi \hbar \text{....} [3]$$

As assumed by Bohr, n_φ is called the angular quantum number. n_r is the radial quantum number.

$$\because P_\varphi = m\, r^2 \dot{\varphi} \quad \therefore \dot{\varphi} = \frac{P_\varphi}{m\, r^2} \text{ ....} [4]$$

$$\int P_r\, dr = \int m\, \dot{r}\, dr = n_r\, h = \int m \frac{dr}{d\varphi} \frac{d\varphi}{dt} dr$$

$$= \int m \frac{P_\varphi}{m\, r^2} \frac{dr}{d\varphi} \frac{dr}{d\varphi}\, d\varphi$$

$$\therefore \int P_r\, dr = P_\varphi \int \left(\frac{1}{r} \frac{dr}{d\varphi} \right)^2 d\varphi \text{ ....[5]}$$

$$\because r = \frac{L}{1+\varepsilon\cos\varphi} = \frac{a\left(1-\varepsilon^2\right)}{1+\varepsilon\cos\varphi}$$

$$\therefore \frac{1}{r} = \frac{1+\varepsilon\cos\varphi}{a\left(1-\varepsilon^2\right)}$$

$$\frac{dr}{d\varphi} = \frac{a\left(1-\varepsilon^2\right)\varepsilon\sin\varphi}{\left(1+\varepsilon\cos\varphi\right)^2}$$

$$\therefore \left(\frac{1}{r} \frac{dr}{d\varphi} \right)^2 = \frac{\varepsilon^2 \sin^2\varphi}{\left(1+\varepsilon\cos\varphi\right)^2}$$

Then, the integral in (5) is given by:

$$I = \int_0^{2\pi} \frac{\varepsilon^2 \sin^2\varphi}{\left(1+\varepsilon\cos\varphi\right)^2} d\varphi \text{ ....[6]}$$

The result of this integral can be obtained by parts as:

$$I = 2\pi \left(\frac{1}{\sqrt{1-\varepsilon^2}} - 1 \right) \text{ ....[7]}$$

Then, equation (5) gives:

$$\frac{2\pi P_\varphi}{\sqrt{1-\varepsilon^2}} \quad 2\pi P_\varphi = n_r h$$

$$\therefore \frac{n_\varphi h}{\sqrt{1-\varepsilon^2}} - n_\varphi h = n_r h$$

$$1-\varepsilon^2 = \frac{n_\varphi^{\;2}}{\left(n_r + n_\varphi\right)^2} = \frac{n_\varphi^{\;2}}{n^2} \quad \ldots[8]$$

Where $n = n_r + n_\varphi$ is called the principal quantum number.

The total energy of the electron is given by:

$$E = \frac{1}{2}m\left[(\dot{r})^2 + (r\dot{\varphi})^2\right] - \frac{z e^2}{r} \ldots\ldots[9]$$

$$\dot{r} = \frac{dr}{d\varphi}\cdot\frac{d\varphi}{dt} = \frac{dr}{d\varphi}\cdot\dot{\varphi}$$

$$\therefore \dot{r} = \frac{P_\varphi}{m r^2}\frac{dr}{d\varphi} \qquad \because \dot{\varphi} = \frac{P_\varphi}{m r^2} \quad \ldots[10]$$

$$(r\dot{\varphi}) = \frac{P_\varphi}{m r} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[11]$$

$$E = \frac{1}{2}m\left[(\dot{r})^2 + (r\dot{\varphi})^2\right] - \frac{z e^2}{r}$$

$$E=\frac{1}{2}m\left[\frac{P_{\varphi}^{2}}{m^{2}r^{4}}\left(\frac{dr}{d\varphi}\right)^{2}+\frac{P_{\varphi}^{2}}{m^{2}r^{2}}\right]-\frac{z\,e^{2}}{r}$$

$$=\frac{P_{\varphi}^{2}}{2m\,r^{2}}\left[\left(\frac{1}{r}\frac{dr}{d\varphi}\right)^{2}+1\right]-\frac{z\,e^{2}}{r}$$

$$\therefore\left(\frac{1}{r}\frac{dr}{d\varphi}\right)^{2}=\frac{2m\,r^{2}E}{P_{\varphi}^{2}}+\frac{2m\,r^{2}z\,e^{2}}{P_{\varphi}^{2}r}-1 \quad [12]$$

But

$$\left(\frac{1}{r}\frac{dr}{d\varphi}\right)^{2}=\frac{\varepsilon^{2}\sin^{2}\varphi}{(1+\varepsilon\cos\varphi)^{2}}$$

$$\because r=\frac{a(1-\varepsilon^{2})}{(1+\varepsilon\cos\varphi)}(1+\varepsilon\cos\varphi)^{2}$$

$$\therefore r'=\frac{a^{2}(1-\varepsilon^{2})^{2}}{r^{2}}$$

$$\varepsilon\cos\varphi=\frac{a(1-\varepsilon^{2})}{r}-1 \;\ldots\ldots\ldots\ldots\ldots\ldots [13]$$

$$\textit{note that}:\cos\varphi=\sqrt{1-\sin^{2}\varphi}$$

$$\varepsilon^{2}(1-\sin^{2}\varphi)=\left[\frac{a(1-\varepsilon^{2})}{r}-1\right]^{2}$$

$$\therefore \varepsilon^2 \sin^2 \varphi = \varepsilon^2 - \left[\frac{a^2(1-\varepsilon^2)^2}{r^2} - \frac{2a(1-\varepsilon^2)}{r} + 1\right] \qquad [14]$$

$$\therefore \left(\frac{1}{r}\frac{dr}{d\varphi}\right)^2 = \frac{r^2\varepsilon^2}{a^2(1-\varepsilon^2)} - 1 + \frac{2r}{a(1-\varepsilon^2)} - \frac{r^2}{a^2(1-\varepsilon^2)} \qquad [15]$$

(12), (15)$\Rightarrow$ (equating the coefficient of r^2)

$$\frac{2mE}{P_\varphi^2} = \frac{-1}{a^2(1-\varepsilon^2)} \qquad \text{.........................[16]}$$

$$\frac{mze^2}{P_\varphi^2} = \frac{1}{a(1-\varepsilon^2)} \qquad \text{.........................[17]}$$

Multiplying (17) by $\frac{1}{a}$, then

$$\frac{2mE}{P_\varphi^2} = \frac{-mze^2}{P_\varphi^2 a}$$

$$\therefore E = \frac{-ze^2}{2a} \qquad \text{..................................[18]}$$

This equation gives the energy in terms of a (see *the case of Bohr*).

Later we can find the energy in terms of the principal quantum number n .

Equations (16), (17) give:

$$E = \frac{-P_\varphi^{\;2}}{2m}\frac{1}{\left(1-\varepsilon^2\right)}\frac{\left(1-\varepsilon^2\right)^2 m^2 z^2 e^4}{P_\varphi^{\;4}}$$

$$\therefore E = -\frac{m z^2 e^4}{2P_\varphi^{\;2}\left(1-\varepsilon^2\right)} \text{......................[19]}$$

But from equation (8) we have:

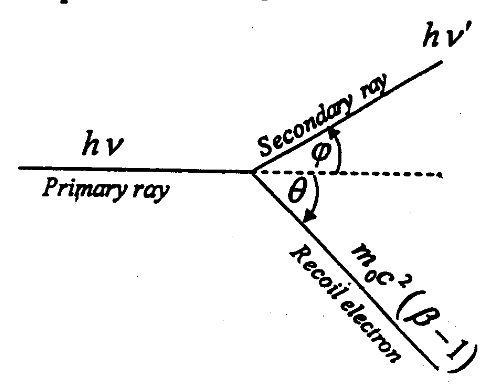
$$\left(1-\varepsilon^2\right) = \frac{n_\varphi^{\;2}}{n^2}, \; ,P_\varphi = n_\varphi \hbar \text{ ....[8]}$$

Then

$$E_n = \frac{-m z^2 e^4}{2n_\varphi^{\;2}\hbar^2}\cdot\frac{n_\varphi^{\;2}}{n^2}$$

$$E_n = -\frac{m z^2 e^4}{2\hbar^2 n^2}$$

The Compton Effect



1 Consider the incident radiation as consisting of photons or light quanta, of energy $h\nu$ traveling in the direction of the primary ray with velocity c.

2. From the theory of relativity, the photon mass $m = h\nu/c^2$ then the momentum $P = h\nu/c$.

3. Suppose this photon strikes a free electron at rest.

4. From the principle of conservation of energy, we get:

$$h\nu = h\nu' + m_0 c^2(\beta - 1) \quad \text{................[1]}$$

Where $m_0 c^2(\beta - 1)$ is the kinetic energy of the electron.

And $\beta = 1/\sqrt{1 - v^2/c^2}$.

5. If we resolve the momentum vectors into two components , we get:

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\varphi + \beta m_0 v\cos\theta \quad \text{.......[2]}$$

$$0 = \frac{h\nu'}{c}\sin\varphi - \beta m_0 \sin\theta \quad \text{..............[3]}$$

To solve these equations let:

$$\alpha = \frac{h\nu}{m_0c^2} = \frac{h}{m_0c\lambda} \quad ,\lambda = \frac{c}{\nu}$$

$$\alpha' = \frac{h\nu'}{m_0c^2} = \frac{h}{m_0c\lambda'}$$

$$b = \sqrt{\beta^2 - 1} = \frac{\beta v}{c} \ or \ \beta = \sqrt{1+b^2}$$

$$l_1 = \cos\varphi \ ,n_1 = \sin\varphi \ ,l_2 = \cos\theta \ ,n_2 = \sin\theta$$

Dividing equation (1) by m_0c^2, we get:

$$\frac{h\nu}{m_0c^2} = \frac{h\nu'}{m_0c^2} + (\beta + 1)$$

$$\therefore \alpha = \alpha' + \sqrt{b^2+1} - 1 \ ....[4]$$

Dividing equations (2), (3) by m_0c, we get:

$$\frac{h\nu}{m_0c^2} = \frac{h\nu'}{m_0c^2}\cos\varphi + \frac{\beta v}{c}\cos\theta$$

$$0 = \frac{h\nu'}{m_0c^2}\sin\varphi - \frac{\beta v}{c}\sin\theta$$

$$\alpha = \alpha' l_1 + b l_2 \ ....[5]$$

$$0 = \alpha' n_1 - b\,n_2 \ ....[6]$$

$$(5) \Rightarrow b^2 l^2 = \alpha^2 - 2\alpha\alpha' l_1 + \alpha'^2 l_1^{\ 2} \ ...[7]$$

$$(6) \Rightarrow \alpha'^2 n_1^{\ 2} = b^2 n_2^{\ 2} \ ....[8]$$

Adding (7), (8)

$$\therefore b^2\left(l_2^2+n_2^2\right)=\alpha^2-2\alpha\alpha' l_1\left(l_1^2 + n_1^2\right)$$

$$\therefore b^2=\alpha^2-2\alpha\alpha' l_1+\alpha'^2 \text{ ....[9]}$$

From (4)

$$b^2=\alpha^2-2\alpha\alpha'+\alpha'^2+2\alpha-2\alpha' \text{....[10]}$$

Subtracting (10), (9), we get:

$$0=2\alpha\alpha'\left(1-l_1\right)-2\alpha+2\alpha'$$

$$0=\alpha\left(1-l_1\right)-\left(\frac{\alpha}{\alpha'}-1\right)$$

$$\therefore \frac{\alpha}{\alpha'}-1=\alpha\left(1-l_1\right) \text{ ....[11]}$$

$$\therefore \frac{\lambda}{\lambda'}-1=\frac{h}{m_0 c\lambda}(1-\cos\varphi)$$

$$\therefore \Delta\lambda=\lambda'-\lambda=\frac{h}{m_0 c}(1-\cos\varphi) \text{ ....[12]}$$

Equation (12) gives the well known expression or the difference in the wave length of the secondary and primary rays $\lambda'-\lambda$.

To get the expression for the kinetic energy of the recoil electron, solve (11) for α'

$$\frac{\alpha}{\alpha'}-1=\alpha\left(1-l_1\right)$$

$$\alpha' = \frac{\alpha}{1+\alpha(1-l_1)} \quad \text{..........................[13]}$$

From equation (4)

$$\alpha = \alpha' + \sqrt{b^2+1} - 1$$

$$\sqrt{b^2+1} - 1 = \alpha - \frac{\alpha}{1+\alpha(1-l_1)}$$

$$= \frac{\alpha^2(1-l_1)}{1+\alpha(1-l_1)}$$

The kinetic energy is given by:

$$E = m_0c^2(\beta - 1)$$

$$= m_0c^2\left[\frac{\alpha^2(1-l_1)}{1+\alpha(1-l_1)}\right]$$

$$E = m_0c^2 \frac{\alpha^2(1-\cos\varphi)}{1+\alpha(1-\cos\varphi)}$$

$$\therefore E = h\nu \frac{\alpha(1-\cos\varphi)}{1+\alpha(1-\cos\varphi)} \quad \text{.............[14]}$$

Where:

$$\sqrt{1+b^2} = \beta, l_1 = \cos\varphi \;\; and \; \alpha = \frac{h\nu}{m_0c^2}.$$

Failure of the old quantum theory

There were obvious weaknesses in the (*old quantum theory*) of Bohr and Sommerfeld. It was seen from the beginning to be a mixture of quantum and classical ideas. The electron was regarded as a point charge and the Sommerfeld rules picked out the allowed orbits which had energies calculated using the classical theory. However, even though classical theory demanded that the accelerating electrons must emit radiation, Bohr postulated that this did not happen for electrons in stationary orbits.

Also, non – periodic phenomena were not included. There was no quantum theory of α particle emission.

Although the Bohr – Sommerfeld theory allowed only integer quantum numbers it was discovered that certain systems demanded half – integer quantum numbers. The explanation of this
Requires a spin structure for the (*particle electron*). In some cases quantitative disagreement occurred between the old quantum theory and experiment and in others even qualitative agreement was not even achieved.

Dissatisfaction with the old quantum theory eventually leads to the discovery of the matrix mechanics of Heisenberg and the equivalent wave mechanics of Schrödinger (1926).

Chapter (2)

Operators, Eigenfunction and Eigenvalues



Operators

An operator is a rule by which, given any function, we have another one.

We may define an operator as multiply the function by the independent variable

$$\xi f(x) = x f(x) \quad \text{.................................... [1]}$$

Another operator δ is the differentiation with respect to the independent variable

$$\delta f(x) = f'(x) \quad \text{.................................... [2]}$$

Linear Operator

An operator $\hat{\alpha}$ is said to be linear if for arbitrary operand u and v

$$\hat{\alpha}(u + v) = \hat{\alpha}u + \hat{\alpha}v \quad \text{.............................. [3]}$$

And for an arbitrary constant c

$$\alpha c \psi = c \hat{\alpha} \psi \quad \text{.. [4]}$$

Among the various mathematical operations that can perform on a function $u(x)$ is:

(i) Differentiation of u be $u'(x)$ with respect to x

(ii) Multiplication of $u(x)$ by x

(iii) Multiplication of $u(x)$ by a constant say c.

$$\left.\begin{aligned}\left[\frac{d}{dx}\right]u(x)&=u'(x)\\ [x]u(x)&=x\,u(x)\\ [c]u(x)&=c\,u(x)\end{aligned}\right\}\text{.............................}[5]$$

The operators $\left[\frac{d}{dx}\right]$, $[x]$ and $[c]$ are usually denoted by $\frac{d}{dx}$, x and c respectively.

The operator symbol must not be confused with symbols representing ordinary functions and numbers. Among the operators of the type c we have the operator I (*I is the unit operator, idem factor or simply unity, which leaves every operand unaltered*) and the operator 0 is the zero operator which annihilates every operand.

If the respective results of operating on u with the operators $\hat{\alpha}$ and $\hat{\beta}$ are add together, then the final result:

$$\hat{\alpha}u + \beta u \text{ is denoted by } \left(\hat{\alpha}+\hat{\beta}\right)u .$$

The expression $\frac{d}{dx}u(x)+x\,u(x)$ is written as:

$$\left[\frac{d}{dx}+x\right]u(x)$$

The notation can be extended to sums of the results of operating on the same operand with more than to operators.

Another convention concerns consecutive operations. If we must operate on u with the operator $\hat{\alpha}$ getting the result $\hat{\alpha}u$ and next operate on this result with the operate $\hat{\beta}$. Then the final result is $\hat{\beta}(\hat{\alpha}u)$ of the two successive operations is usually denoted by $\hat{\beta}\hat{\alpha}u$.

For example if we first operate on $u(\alpha)$ with the operator x getting $x\,u(x)$ and next operate on the result with $\frac{d}{dx}$, then the final result $\frac{d}{dx}[x\,u(x)]$ must be written in the convention notation $\frac{d}{dx}x\,u(x)$, on the other hand if the order of operations is reversed the final result would be $x\left(\frac{d}{dx}\right)u(x)$.

By the result of differentiation

$$\left(\frac{d}{dx}\right)\left[x\,u(x)\right]=u(x)+x\,\frac{d}{dx}u(x)\ .....[6]$$

And

$$x\left(\frac{d}{dx}\right)u(x)=x\,\frac{d}{dx}u(x)\ ....[7]$$

Therefore:

$$\left(\frac{d}{dx}\right)x\,u(x)\neq x\left(\frac{d}{dx}\right)u(x)$$

$$\left(\frac{d}{dx}\right)x-x\left(\frac{d}{dx}\right)\neq 0\ ....[8]$$

The inequality (8) illustrates the importance of the remembering the order in which the individual operations must be carried out when the conventional notation is used for successive operation .

Commutators

The operator $\hat{\alpha}\hat{\beta}-\hat{\beta}\hat{\alpha}$ called the commutator of the operators $\hat{\alpha}$ and $\hat{\beta}$ it is also written as $[\alpha,\beta]$

$$\left[\hat{\alpha},\hat{\beta}\right]=\hat{\alpha}\hat{\beta}-\hat{\beta}\hat{\alpha}\ ....[9]$$

The commutator $\left[\hat{\alpha},\hat{\beta}\right]$ satisfies the following identities:

$$\left[\hat{\alpha},\hat{\beta}\right]=\hat{\alpha}\hat{\beta}-\hat{\beta}\hat{\alpha}\ ....[10]$$

$$\left[\hat{\alpha},\hat{\beta}\hat{\gamma}\right]=\left[\hat{\alpha},\hat{\beta}\right]\hat{\gamma}+\hat{\beta}\left[\hat{\alpha},\hat{\gamma}\right] \quad \text{.................[11]}$$

$$\left[\hat{\alpha}\hat{\beta},\hat{\gamma}\right]=\left[\hat{\alpha},\hat{\gamma}\right]\hat{\beta}+\hat{\alpha}\left[\hat{\beta},\hat{\gamma}\right] \quad \text{.................[12]}$$

$$\left[\alpha,[\beta,\gamma]\right]+\left[\beta,[\gamma,\alpha]\right]+\left[\gamma,[\alpha,\beta]\right] \quad \text{.....[13]}$$
$$=0$$

That is readily deduced from the definition (9).

Example (1):

Find the explicit expressions for the following operators:

(i) $\left(\frac{d}{dx}+x\right)^2$ (ii) $\left(\frac{d}{dx}x\right)^2$

Solution

(i) Applying the operator twice to an arbitrary function ψ we get:

$$\left(\frac{d}{dx}+x\right)\left(\frac{d\psi}{dx}+x\,\psi\right)=\frac{d^2\psi}{dx^2}+2x\frac{d\psi}{dx}+x^2\psi+\psi$$

And consequently,

$$\left(\frac{d}{dx}+x\right)^2=\frac{d^2}{dx^2}+2x\frac{d}{dx}+x^2+1$$

(ii)

$$\left(\frac{d}{dx}x\right)\left(\frac{d}{dx}x\,\psi\right)=\left(\frac{d}{dx}x\right)\left(x\,\frac{d\psi}{dx}+\psi\right)$$

$$=\frac{d}{dx}\left(x^{2}\frac{d\psi}{dx}+x\,\psi\right)$$

$$=\left(x^{2}\frac{d^{2}}{dx^{2}}+3x\,\frac{d}{dx}+1\right)\psi$$

And consequently,

$$\left(\frac{d}{dx}x\right)^{2}=x^{2}\frac{d^{2}}{dx^{2}}+3x\,\frac{d}{dx}+1$$

Example (2):

Find the commutations relations for the following operators

(i) x and $\frac{d}{dx}$ (ii) $\frac{\partial}{\partial\varphi}$ and $f\,(r,\theta,\varphi)$

Solution

(i) Applying the operator $\frac{d}{dx}x\;,x\,\frac{d}{dx}$ to an arbitrary function ψ, we get:

$$\left(\frac{d}{dx}x\;-x\,\frac{d}{dx}\right)\psi=\frac{d}{dx}(x\,\psi)-x\,\frac{d\psi}{dx}=\psi$$

or

$$\frac{d}{dx}x - x\frac{d}{dx} = 1 \quad \therefore \left[\frac{d}{dx}, x\right] = +1$$

(ii)

$$\left(\frac{\partial}{\partial\varphi}f - f\frac{\partial}{\partial\varphi}\right)\psi = \frac{\partial}{\partial\varphi}(f\psi) - f\frac{\partial\psi}{\partial\varphi}$$

$$= \left(\frac{\partial f}{\partial\varphi}\right)\psi$$

$$\frac{\partial}{\partial\varphi}f - f\frac{\partial}{\partial\varphi} = \frac{\partial f}{\partial\varphi} \quad \therefore \left[\frac{\partial}{\partial\varphi}, f\right] = \frac{\partial f}{\partial\varphi}$$

Example (3):

Find the translation operator that are maps $\psi(x)$ into $\psi(x+a)$.

Solution

Let us define the sought operator by the equality:

$$T_a\psi(x) = \psi(x+a)$$

We then press $\psi(x+a)$ as a power series in a:

$$\psi(x+a) = \psi(x) + a\frac{d\psi}{dx} + \frac{a^2}{2!}\frac{d^2\psi}{dx^2} + \cdots$$

$$= \sum_{n=0}^{\infty}\frac{a^n}{n!}\frac{d^n}{dx^n}\psi(x)$$

Noting that $\sum_{n=0}^{\infty}\frac{x^n}{n!} = e^x$ we get:

$$\hat{T}_a = e^{a\frac{d}{dx}}$$

Eigenfunctions and Eigenvalues

If for a specific value λ_i of the numerical constant λ, a operand u_i satisfied the equation:

$$\hat{\alpha} u_i = \lambda u_i$$

Where λ is the eigenvalue of the given operator $\hat{\alpha}$ then:

$$\hat{\alpha} u_i = \lambda_i u_i$$

Then we say that the number λ_i is the eigenvalue of the operator α, and that the operand u_i is an eigenfunction of α, and that the eigenvalue λ_i and eigenfunction u_i of the operator α belong to each other.

For example

The function $(\sin(3x))$ we have:

$$\left(-\frac{d^2}{dx^2}\right)\sin(3x) = 9\sin(3x)$$

We say that the number 9 is an eigenvalue of the operator $\left(-\frac{d^2}{dx^2}\right)$ and $(\sin(3x))$ is the eigenfunction of this operator.

We can restate the definition of eigenfunction and eigenvalue thus, an eigenfunction of the operator $\hat{\alpha}$, is an operand such that operating on it with $\hat{\alpha}$ is equivalent to multiplying it by a numerical constant this constant then being corresponding eigenvalue of α.

If $\hat{\alpha} = -\frac{d^2}{dx^2}$ the according to equation $\hat{\alpha}u = \lambda u$

We have to find the eigenvalue and eigenfunction of deferential operator $\left(-\frac{d^2}{dx^2}\right)$.

Any positive number, zero included is an eigenvalue of the operator $\left(-\frac{d^2}{dx^2}\right)$ and the eigenfunction of $\left(-\frac{d^2}{dx^2}\right)$ belonging to the eigenvalue λ.

The totality of the eigenvalues of an operator is called its "eigenvalue-*spectrum*" of simply its spectrum.

For example we say that the spectrum of an operator $\left(-\frac{d^2}{dx^2}\right)$ consist of all positive numbers, zero included consider a differential equation

$$\frac{d^2y}{dx^2}+\lambda y = 0 \qquad [14]$$

Suppose we want to find a regular solution $y(x)$ i.e. a solution such that $y, \frac{dy}{dx}, \frac{d^2y}{dx^2}$ are continuous in the domain:

$$0 \le x \le \pi \qquad [15]$$

And that y satisfies the boundary conditions.

$$y(0)=0 \qquad [16]$$

$$y(\pi)=0 \qquad [17]$$

And λ is a parameter independent of x.

The most general solution of the equation (14) is:

$$y = a\sin\sqrt{\lambda}x + b\cos\sqrt{\lambda}x$$

Condition (16) gives $b = 0$

the solution therefore is:

$$y = a\sin\sqrt{\lambda}x \qquad [18]$$

Condition (17) requires that $y = a\sin\sqrt{\lambda}\pi = 0$

$$\therefore \sin\sqrt{\lambda}\,\pi = 0 \qquad [19]$$

It is possible only when $\sqrt{\lambda}$ is an integer $n \geq 1$

$$\therefore \lambda = n^2 \quad ,(n = 1,2,3,\cdots) \qquad [20]$$

We see that the problem given above in general has no solution except when the parameter λ has one of the discrete set of values $1^2, 2^2, 3^3, \cdots$

The discrete numbers are the eigenvalue of the differential operator D^2 and the corresponding solution:

$$y_n = a_n \sin nx \quad ,(n = 1,2,3,\cdots) \qquad [21]$$

are the eigenfunction of the equation and the eigenvalue spectrum of the equation is:

$$1^2, 2^2, 3^3, \cdots$$

In quantum mechanics the eigenfunctions allowed are chosen from the class of functions which are single-valued and continuous-except at a finite number of points where the function may become infinite – in the complete range of the variables and which give a finite result when the square of their absolute values are integrated over the complete range of variables.

If ψ is such a function, and ψ^* its complex conjugate the condition mentioned earlier requires that $\int \psi\psi^* d\tau$ be definite.

i.e $\int |\psi|^2 d\tau$

Hermition Operators:

If ψ and φ are any two functions and $\hat{\alpha}$ is an operator operating on ψ and φ. $\hat{\alpha}$ is said to be hermition if:

$$\int \psi^* \varphi^* (\hat{\alpha}\psi) d\tau = \int \psi (\hat{\alpha}^* \varphi^*) d\tau \quad \text{..........[22]}$$

Theorem (1)

The eigenvalues for functions of the hermition operators are always real.

Proof

If $\hat{\alpha}$ is an Hermition operator and ψ is an eigenfunction of $\hat{\alpha}$ with eigenvalue a then

$$\hat{\alpha}\psi = a\psi \quad \text{..........[23]}$$

$$\alpha^* \psi^* = a^* \psi^* \quad \text{..........[24]}$$

$$\begin{aligned} \int \psi^* (\hat{\alpha}\psi) d\tau &= \int \psi^* a \psi d\tau \\ &= a \int \psi^* \psi d\tau \end{aligned} \quad \text{..........[25]}$$

and

$$\int \psi\left(\alpha^{*}\psi^{*}\right)d\tau = \int \psi\left(a^{*}\psi^{*}\right)d\tau$$
$$= a^{*}\int \psi\psi^{*}\,d\tau \quad \text{................[26]}$$

if $\hat{\alpha}$ is hermition,

$$\int \psi^{*}\hat{\alpha}\psi\,d\tau = \int \psi\left(\hat{\alpha}^{*}\psi^{*}\right)d\tau$$

$$\therefore a = a^{*}$$

which is true only when "a" is real.

Theorem (2)

The eigenfunctions of any hermition operator are orthogonal functions in the interval corresponding to the complete range of variables.

Proof

Let the operator be $\hat{\alpha}$ and the eigenfunctions ψ_1, ψ_2 with eigenvalues a_1 and a_2 so that:

$$\hat{\alpha}\psi_1 = a_1\psi_1$$
$$and \quad \hat{\alpha}\psi_2 = a_2\psi_2 \quad , a_1 \neq a_2 \quad \text{................[27]}$$

Now consider the integral,

$$\int \psi_2^{*}\hat{\alpha}\psi_1\,d\tau = a_1\int \psi_2^{*}\psi_1\,d\tau \quad \text{...................[28]}$$

Since $\hat{\alpha}$ is hermition, we have:

$$\int \psi_2^{*}\hat{\alpha}\psi_1\,d\tau = \int \psi_1\hat{\alpha}^{*}\psi_2^{*}\,d\tau$$
$$= a_2^{*}\int \psi_1\psi_2^{*}\,d\tau$$

$$\int \psi_2^* \hat{\alpha} \psi_1 \, d\tau = a_2 \int \psi_1 \psi_2^* \, d\tau \quad \text{....................[29]}$$

$a_2^* = a_2$ because $\hat{\alpha}$ being hermition its eigenvalues are real.

$$a_1 \int \psi_2^* \psi_1 \, d\tau = a_2 \int \psi_1 \psi_2^* \, d\tau$$

$$\therefore (a_1 - a_2) \int \psi_1 \psi_2^* \, d\tau = 0$$

$\because a_1 \neq a_2$ then,

$$\int \psi_1 \psi_2^* \, d\tau = 0$$

Therefore the eigenfunctions belonging to different eigenvalues of any Hermition operator are orthogonal.

Eigenfunctions of Commuting Operators

In most problems in atomic and nuclear structure we come across several operators at the same time. The eigenfunctions of one operator are usually different from those of another operator, but when the operators commute an important exception is seen and that is we can get one set of functions which is set of eigenfunctions of two operators at the same time.

Theorem: (3)

If two operators $\hat{\alpha}$ and $\hat{\beta}$ commute there exists a set of functions which are simultaneously eigenfunctions of both the operators $\hat{\alpha}$ and $\hat{\beta}$.

Example:

Find the eigenfunctions and eigenvalues for the operators:

(i) $i\dfrac{d}{dx}$ (ii) $\dfrac{d}{d\varphi}$

Solution

(i) Applying the operator to an arbitrary function ψ we get:

$$i\frac{d\psi}{dx}=\lambda\psi$$

there λ λ is the eigenvalue corresponding to the eigenfunction ψ.

Integrating we have

$$\psi(x)=Ce^{-i\lambda x}$$

where C is a constant, and λ is a real number (*a continuous spectrum*).

The finiteness of $\psi(x)$ as x tends to zero.

(ii) $\dfrac{d\psi}{d\varphi}=\lambda\psi \Rightarrow \dfrac{d\psi}{\psi}=\lambda d\varphi \Rightarrow \psi=Ce^{\lambda\varphi}$

Because our eigenfunction must be single – valued the solution must satisfy the condition

$$\psi(\varphi)=\psi(\varphi+2\pi)$$

Substituting the original solution, we fined λ from the condition:

$$e^{2\pi\lambda}=1$$

thus $\lambda = i\,m$ where $m = 0, \pm 1, \pm 2$

Problems on chapter II

1. Find the explicit form of the following operators:

$$\left(\frac{d}{dx}+x\right)^2, \quad \left(\frac{d}{dx}+\frac{1}{x}\right)^2$$

$$\left(x\frac{d}{dx}\right)^2, \quad \left(\frac{d}{dx}x\right)^2$$

2. Prove that:

$$\left[\hat{\alpha},\hat{\beta}\hat{\gamma}\right]=\left[\hat{\alpha},\hat{\beta}\right]\hat{\gamma}+\hat{\beta}\left[\hat{\alpha},\hat{\gamma}\right],$$

$$\left[\hat{\alpha}\hat{\beta},\hat{\gamma}\right]=\left[\hat{\alpha},\hat{\gamma}\right]\hat{\beta}+\hat{\alpha}\left[\hat{\beta},\hat{\gamma}\right],$$

$$\left[\alpha,\left[\beta,\gamma\right]\right]+\left[\beta,\left[\hat{\gamma},\hat{\alpha}\right]\right]+\left[\gamma,\left[\hat{\alpha},\hat{\beta}\right]\right]=0,$$

$$\left[\hat{A},\frac{1}{\hat{B}}\right]=-\frac{1}{\hat{B}}\left[\hat{A},\hat{B}\right]\frac{1}{\hat{B}}$$

3. Prove that:

$$\left[x,\frac{d}{dx}\right]=-1$$

$$\left[\hat{P}_x,\hat{x}\right]=-i\,\hbar \qquad \left[\hat{P}_x,\hat{Y}\right]=-i\,\hbar\delta$$

where $P_x = -i\hbar \frac{\partial}{\partial x}$

4. Show that if $\hat{\alpha}, \hat{\beta}$ commute, and if ψ is eigenfunction of $\hat{\alpha}$ belonging to the eigenvalue λ, then $\hat{\beta}\psi$ is also an eigenfunction of $\hat{\alpha}$ belonging to the eigenvalue λ.

Chapter (3)

Schrodinger waver equation

The Basic Postulates of Quantum Mechanics

The experiments exhibiting the duality of matter such as Davisso - Germer's experiment, and Thomson's electron diffraction experiment can be explained by assuming that with each bit of matter there is associated a new type of field represented by a symbol ψ and that this field has wave like character, The de Broglie wavelength of this matter wave is given by:

$$\lambda = h/mv$$

These ψ waves intimately associated with the particles to which they belong and the behavior of the particles is found to be predictable only with the knowledge of the ψ waves at any instant.

In the case of mechanical vibrations the wave-function simply gives the displacement from the equilibrium position of every point of the system. The physical interpretation of the ψ function is less obvious.

Max Born has postulated that,

$$\int \psi^* \psi \, d\tau = \int |\psi|^2 \, d\tau$$

is the probability of finding the particle at a point in the volume element $d\tau$ given by the coordinates .

Therefore $|\psi|^2$ is the probability density.

Born's hypothesis leads to consequences which are in excellent agreement with the experimental results, e.g., when applied to the scattering of alpha particles by an atomic nucleus, it yields the Rutherford Scattering formula.

Wave mechanics explains the dependence of the probability density distribution of the electron in the atom. It does not give any clue to the nature of the orbits of the electron. Like E and H the ψ function is not itself observable, it is a tool for calculation. Since it gives results that are in agreement with experiments it has a certain degree of reality.

The basic postulates of quantum mechanics give rules for:

(1) Calculating for any system the complete wave function $\psi(x, y, z, t)$,

(2) Calculating the expected value of the observable quantities the distance x , momentum P and total energy E , etc, are dynamical variables .

In classical mechanics the dynamical variables play an altogether new role. They are converted by a set of rules into mathematical operators which then operate on the wave function ψ. We shall formulate these rules like axioms in geometry by making certain postulates. The theory follows these postulates.

Let us consider a system of particles of f degrees of freedom which could be descried classically at a given time "t" by their coordinates $q_1, q_2, \cdots, q_r$ and the corresponding conjugate momentum $P_1, P_2, \cdots P_r$.

Postulate (1)

Any state of the system is described as fully as possible by a function $\psi(q_1, q_2, \cdots, q_r, t)$ class Q. ψ is called the state function of the system and has the property that $\int \psi \psi^* d\tau$ is the probability that the variables lie in the volume element $d\tau$ at time t. Since each variable must have some value the total probability must be unity, so that

$$\int \psi^*(q_1, q_2, \cdots, q_r) \psi(q_1, q_2, \cdots, q_r) d\tau = 1 \qquad [1]$$

Where the integral is taken over all possible values of the q's.

Postulate (2)

To every dynamical variable M there is corresponding linear Hermition operator $\hat{\mu}$. The rules for finding these operators are the following:

(i) If M is one of the q's or t the operator is multiplication by the variable itself.

(ii) If M is one of the P's the operator is

$$P = \frac{h}{2\pi i}\frac{\partial}{\partial q} = \frac{\hbar}{i}\frac{\partial}{\partial q}$$

Where q's is conjugate to P's and $\hbar = h/2\pi$

(iii) If M any dynamical variable which can be expressed in terms q's and P's and t, the operator is found by substituting the operators for the q's the P's and t as defined above in the algebraic expression for M, and replacing the ordinary processes of algebra by those of operator algebra.

Postulate (3)

The state function $\psi(q,t)$ is an eigenfunction of the operator $\hat{\alpha}$ corresponding to a dynamical variable M, then

$$\hat{\alpha}\psi(q_1,t) = m\,\psi(q,t)\ldots\ldots\ldots\ldots\ldots\ldots[2]$$

And in this state the variable M has a constant value m. Such a state is known as the eigenstate of M.

Postulate (4)

The state function $\psi(q_1,t)$ satisfy the equation

$$H\left(q,\frac{\hbar}{i}\frac{\partial}{\partial q},t\right) = \frac{-\hbar}{i}\frac{\partial}{\partial t}\psi(q_1,t)\ldots\ldots\ldots[3]$$

Where $H\left(q,\frac{\hbar}{i}\frac{\partial}{\partial q},t\right)$ is the Hamiltonian operator for the system.

Schrödinger's Wave Equation

If the state functions is an eigenfunction of the energy operator H, with an eigenvalue E then $\psi(q_1 t)$ satisfies the equation

$$H\left(q,\frac{\hbar}{i}\frac{\partial}{\partial q},t\right)\psi(q,t) = E\psi(q,t)\ldots\ldots\ldots[4]$$

Postulate (4) states that

$$H\left(q,\frac{\hbar}{i}\frac{\partial}{\partial q},t\right)\psi(q,t) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\psi(q,t)$$

If the two equations above are to be consistent, $\psi(q_1,t)$ must be of the form

$$\psi(q,t)=\psi(q)e^{-\frac{i}{k}Et} \text{ ....[5]}$$

Where $\psi(q)$ is the solution of the equation,

$$H\left(q,\frac{\hbar}{i}\frac{\partial}{\partial q},t\right)\psi(q)=E\psi(q) \text{ ....[6]}$$

Equation (6) is Schrödinger's equation for a stationary state. i.e. for a state which is eigenstate of the energy operator.

The formation of the wave equation by the "*operator substitution* "method though appearing arbitrary, certainly indicates some meaningful link between the classical mechanics and Schrödinger wave mechanics. The wave like nature of matter was already beginning to be appreciated even before Schrödinger put forth his theory. His wave equation is similar to the familiar wave equation of the classical theory. It would therefore be helpful in understanding the new wave mechanics if the Schrödinger's wave equation is derived firstly as a continuity of the classical wave equation and then by the working of the postulate of quantum mechanics on the different kinetic variables.

Schrödinger's Wave Equation From the Wave Equation of Light

Consider the differential equation of the wave equation in optics

$$\nabla^2\varphi = \frac{1}{u^2}\frac{\partial^2\varphi}{\partial t^2} \qquad \text{.......[7]}$$

Where u is the phase velocity of light in the medium. Since φ is periodic in time we can write.

$$\varphi(x,y,z,t) = \psi(x,y,z)e^{2\pi i\gamma t} \qquad \text{.......[8]}$$

Where γ is the frequency of light, we get

$$\nabla^2\psi = -\frac{4\pi^2\gamma^2}{u^2}\psi = -\frac{4\pi^2}{\lambda^2}\psi$$

$$\therefore \nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0 \qquad \text{.......[9]}$$

At this state we induct the de Broglie wave associated with a particle of mass m moving with a velocity u in conservative field of force having potential $v(x,y,z)$ the wavelength of de Broglie wave.

$$\lambda = \frac{h}{mv}$$

$$\frac{1}{\lambda^2} = \frac{m^2v^2}{h^2} \qquad \text{.......[10]}$$

Kinetic energy

$$\frac{1}{2}mv^2 = T = E - V$$

where E is the total energy

$$mv^2 = 2m(E - V)$$

$$\therefore \frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [11]$$

Substituting them in (9) we get the Schrödinger's wave equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots [12]$$

Schrödinger's Wave Equation By Operator Substituting Method

As an illustration as to how the " *operator substitution* " method also leads to the Schrödinger's wave equation , let us consider a system consisting of a particle of mass m moving in a potential field$V(x, y, z)$. The kinetic energy of the particle

$$T = \frac{1}{2m}\left(P_x^{\,2} + P_y^{\,2} + P_z^{\,2}\right)$$

Therefore the classical Hamiltonian will be

$$H = \frac{1}{2m}\left(P_x^{\,2} + P_y^{\,2} + P_z^{\,2}\right) + V(x, y, z) \; [13]$$

According to the postulate (4) the Hamiltonian operator

$$H\left(q,\frac{\hbar}{i},\frac{\partial}{\partial q},t\right)=\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2+\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)^2+\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)^2\right]$$
$$+V\,(x,y,z)$$

$$H\left(q,\frac{\hbar}{i},\frac{\partial}{\partial q},t\right)=-\frac{\hbar^2}{2m}\nabla^2+V\,(x,y,z)\;.......[14]$$

The Schrödinger's equation including time

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z,t)+V\,\psi(x,y,z,t)$$
$$=-\frac{\hbar}{i}\frac{\partial}{\partial t}\psi(x,y,z,t)\quad ..[15]$$

If the solution of equation (15) is

$$\psi(x,y,z,t)=\psi(x,y,z)e^{-\frac{i}{\hbar}Et}$$

We obtain the equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V\,(x,y,z)\right]\psi(x,y,z)=E\psi(x,y,z)$$

$$\therefore\frac{\hbar^2}{2m}\nabla^2\psi+(E-V)\psi=0$$

$$\nabla^2\psi+\frac{2m}{\hbar^2}(E-V)\psi=0.\;.....................[16]$$

which is the same as (12)

From the postulated form of operators for position and momentum Heisenberg discovered an important rule for their product. Since

$$pq\psi = \frac{\hbar}{i}\frac{\partial}{\partial q}(q\psi) = \frac{\hbar}{i}\psi + \frac{\hbar}{i}q\frac{\partial\psi}{\partial q} \text{........[17]}$$

and

$$q\,p\psi = q\left(\frac{\hbar}{i}\frac{\partial}{\partial q}\psi\right) = \frac{\hbar}{i}q\frac{\partial\psi}{\partial q} \text{[18]}$$

we have the result

$$(pq - qp)\psi = \frac{\hbar}{i}\psi \text{..................................[19]}$$

The Amplitude Equation

Let us first consider a Newtonian system with one degree of freedom, consisting of a particle of mass m restricted to motion along a fixed straight line which we take as the x – axis and potential energy $V(x)$ through out the system $-\infty < x < \infty$.

For this system we have the Schrödinger wave equation thus.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(x,t) \text{..[20]}$$

In order to solve the equation (20) we have to study the solution Ψ which can be expressed as the product of two functions one involving the time alone and the other the coordinate alone.

We propose such a solution

$$\Psi(x,t)=\psi(x)\varphi(t) \qquad \text{[21]}$$

$$\therefore \frac{\partial^2\Psi}{\partial x^2}=\varphi(t)\frac{\partial^2\Psi}{\partial x^2}$$

And

$$\frac{\partial\Psi}{\partial t}=\psi(x)\frac{\partial\varphi}{\partial t} \qquad \text{[22]}$$

Substituting these values in (20), we get

$$-\frac{\hbar^2}{2m}\varphi(t)\frac{d^2\psi}{dx^2}+V(x)\psi(x)\varphi(t)=-\frac{\hbar}{i}\psi(x)\frac{d\varphi}{dt} \qquad \text{[23]}$$

Divide the equation (23) by $\psi(x)\varphi(t)$ we get,

$$\frac{1}{\psi(x)}\left\{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi(x)\right\}=-\frac{\hbar}{i}\frac{i}{\varphi(t)}\frac{d\varphi}{dt} \qquad \text{[24]}$$

The right side of this equation is a function of time alone and the left side a function of the coordinate x

alone. Therefore it is necessary that the value of the quantity to which each side is equal to be dependent neither on x nor on t. This constant quantity is the total energy E.

$$\therefore -\frac{\hbar}{i}\frac{1}{\varphi(t)}\frac{d\varphi}{dt} = E$$

$$\therefore \frac{d\varphi}{dt} = -\frac{\hbar}{i}E\varphi(t) \quad \text{.................................[25]}$$

And

$$\frac{1}{\psi(x)}\left\{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x)\right\} = E$$

$$\therefore -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\{E - V(x)\}\psi = 0 \quad \text{............[26]}$$

It is found that the equation (26) possesses various, satisfactory solutions corresponding to the values of the constant E. Let us indicate the values of E by a subscript n and represent the amplitude function corresponding to E_n by $\psi_n(x)$. The equation (25) can be integrated,

$$\frac{d\varphi}{dt} = -\frac{i}{\hbar} E\varphi(t) \quad \Rightarrow \frac{d\varphi}{\varphi} = -\frac{i}{\hbar} E\, dt$$

$$\log_e \varphi(t) = -\frac{i}{\hbar} E\, t$$

$$\therefore \varphi_n(t) = e^{-(i/\hbar)E_n t} \quad \text{.........} [27]$$

The general solution of equation (20) is the sum of all the particular solution with arbitrary coefficients. Therefore:

$$\Psi(x,t) = \sum_n a_n \Psi_n(x,t)$$
$$= \sum_n a_n \psi_n(x) e^{-(i/\hbar)E_n t} \quad \text{.........} [28]$$

The wave equation satisfied by ψ^* is the complex conjugate of equation (20) namely.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi^*(x,t) + V^*(x)\Psi^*(x,t)$$
$$= -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi^*(x,t) \quad .[29]$$

The general solution of this conjugate wave equation is the following, the conjugate of (28)

$$\Psi^*(x,t) = \sum_n a_n^* \Psi_n^*(x,t)$$
$$= \sum_n a_n^* \psi_n^*(x) e^{-(i/\hbar)E_n t} \quad \text{.........} [30]$$

Physical Interpretation of Wave Functions

The essential feature of the quantum theory is the wave function ψ which is the solution of the wave equation. This is expected to provide a complete description of the behavior of the particle of mass m with the potential energy $V\left(r,t\right)$ therefore it is analogous to the classical trajectory $r\left(t\right)$. It follows that any result of an experiment performed upon the system can be interpreted and explained correctly if the wave function is known.

Since the interpretation of ψ has to be in probabilistic manner it has to be interpreted in statistical terms.

Probably for this reason Max Born has introduced the concept of probability density for a particle in a system.

One can imagine an ensample of identical and non-integrating systems each consisting of a free particle with a potential energy in the three-dimensional configurationally space and each described by the same wave function $\psi\left(r,t\right)$.

Born has assumed that the numerical results of the measurement at a particular time "t "of any physically meaningful quantity such as position, momentum or energy, will in general not be the same for the entire region.

Rather there will be a distribution of these numbers that can be described by a probability function, the probability density being.

$$P(r,t) = |\psi(r,t)|^2 \text{ ....} [1]$$

The probability of finding the particle somewhere in the region specified earlier must be unity so that

$$\int |\psi(r,t)|^2 d\tau = 1 \text{ ....} [2]$$

The time derivative of the integral of P over a fixed volume V will give an idea of the probability current density:

$$\frac{\partial}{\partial t} \int_V P(r,t) d\tau = \int_V \left(\psi^* \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \right) d\tau \text{ ..} [3]$$

Since,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

We get,

$$\frac{\partial}{\partial t}\int_V P(r,t)\,d\tau = \int_V \left[\psi^* \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi - \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi\psi^*\right] d\tau$$

$$= \frac{i\hbar}{2m}\int_V \left[\psi^*\nabla^2\psi - \left(\nabla^2\psi^*\right)\psi\right] d\tau$$

$$= -\frac{\hbar}{2mi}\int_V \nabla\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] d\tau$$

$$\frac{\partial}{\partial t}\int_V P(r,t)\,d\tau = \frac{i\hbar}{2m}\int_A \left[\psi^*\nabla\psi - \psi\nabla\psi^*\right]_n dA \quad [4]$$

The last integral is obtain by using Green's Theorem where A is the bounding surface of the region of integration and $[\;]_n$ denotes the components of the vector in brackets in the direction of the outward normal to the surface element dA.

We define a vector $i(r,t)$

$$\underline{J}(r,t) = \frac{\hbar}{2i\,m}\left[\psi^*\underline{\nabla}\psi - \psi\underline{\nabla}\psi^*\right]$$

$$J(x,t) = \frac{\hbar}{2i\,m}\left[\psi^*\psi' - \psi\psi^{*\prime}\right]$$

Then

$$\frac{\partial}{\partial t}\int_V P(r,t)\,d\tau = -\int_V (\underline{\nabla}\cdot\underline{J})\,d\tau = -\int_A J_n\,dA \qquad [5]$$

In the case of the wave packet, ψ vanishes at great distance, the surface integral is evidently zero when the volume V covers the entire space, from (5) we get,

$$\frac{\partial}{\partial t}P(r,t)+\underline{\nabla}\cdot\underline{J}=0 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots [6]$$

$$\underline{J}=\frac{\hbar}{2i\,m}\left(\psi^{*}\psi'-\psi\psi^{*\prime}\right)$$

$$\underline{J}=\frac{\hbar}{2i\,m}\begin{vmatrix}\psi^{*} & \psi\\ \psi^{*\prime} & \psi'\end{vmatrix}=\frac{\hbar}{2i\,m}W\left[\psi^{*},\psi\right]$$

Equation (6) is of the form of the equation describing the conservation of the flow of the fluid of density P and current density S when there are no sources or sinks. By analogy we can interpret $J(r,t)$ in (6) as "*probability current density*"

$$\textit{momentum} \qquad P\rightarrow -i\hbar\nabla$$

$$\textit{the velocity} \quad v=\frac{P}{m}\rightarrow\frac{-i\hbar}{m}\nabla=\frac{\hbar}{im}\nabla$$

which is the velocity operator.

The Expectation Value:

The expectation value of an operator is the mathematical expectation for the result of a single measurement, or it is the average of the results of a large number of measurements on independent systems described.

We write the expectation value of r as

$$<r>=\int \psi^* r \psi \, d\tau \quad \text{.................................[1]}$$

where ψ is normalized. Also the expectation value of the potential energy is

$$<V>=\int \psi^* V \psi \, d\tau \quad \text{.................................[2]}$$

and

$$<E>=<\frac{P^2}{2m}>+<V> \quad \text{.........................[3]}$$

In terms of the differential operators

$$<i\hbar\frac{\partial}{\partial t}>=<-\frac{\hbar^2}{2m}\nabla^2>+<V> \quad \text{............[4]}$$

equation (4) is consistent with the wave equation

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{-\hbar^2}{2m}\nabla^2\psi+V\psi \quad \text{........................[5]}$$

We can, also, write the expectation value of the energy and the momentum as

$$<E>=\int \psi^{*} i\hbar \frac{\partial \psi}{\partial t} d\tau \text{ .... [6]}$$

$$<P>=\int \psi^{*}(-\hbar) \frac{\partial \psi}{\partial x} dx \text{ .... [7]}$$

or

$$<P>=\int \psi^{*}(i\hbar) \operatorname{grad} \psi \, d\tau \text{ .... [8]}$$

Time Dependence of Expectation Value:

We shall postulate that the expectation value of a dynamical variable $\hat{F}$ in a certain state is always given by

$$<\hat{F}>=\int \psi^{*} \hat{F} \psi \, d\tau \text{ .... [1]}$$

Let us take the time derivative of $<\hat{F}>$

$$\frac{d}{dt}<\hat{F}>=\int\left[\frac{\partial \psi^{*}}{\partial t} \hat{F} \psi+\psi^{*} \hat{F} \frac{\partial \psi}{\partial t}\right] d\tau \text{ .. [2]}$$

$$\therefore \hat{H} \psi=i\hbar \frac{\partial \psi}{\partial t}$$

$$\therefore \frac{\partial \psi}{\partial t}=\frac{1}{i\hbar} \hat{H} \psi \quad , \frac{\partial \psi^{*}}{\partial t}=-\frac{1}{i\hbar}(\hat{H} \psi)^{*} \text{ ... [3]}$$

and since $\hat{H}$ is hermitian operator, then

$$\int \psi^* H \psi \, d\tau = \int (H\psi)^* \psi \, d\tau = \int \psi H^* \psi^* \, d\tau \qquad \text{..................[4]}$$

Using (3), (4) equation (2) gives

$$\frac{d}{dt} < \hat{F} >= \int \left[-\frac{1}{i\hbar} \psi^* \hat{H} \hat{F} \psi + \psi^* \frac{\partial F}{\partial t} \psi + \frac{1}{i\hbar} \hat{F} \hat{H} \psi \right] d\tau$$

$$\frac{d}{dt} < \hat{F} >= \int \psi^* \left[\frac{\partial \hat{F}}{\partial t} + \frac{1}{i\hbar} \left(\hat{F}\hat{H} - \hat{H}\hat{F} \right) \right] \psi \, d\tau$$

$$= \int \psi^* \left\{ \frac{\partial \hat{F}}{\partial t} + \frac{1}{i\hbar} \left[\hat{F}, \hat{H} \right] \right\} \psi \, d\tau$$

$$\frac{d}{dt} < \hat{F} >=< \frac{\partial \hat{F}}{\partial t} > + \frac{1}{i\hbar} < \left[\hat{F}, \hat{H} \right] \qquad \text{..........[5]}$$

if $< \hat{F} >= \hat{F}$, i ,e if only one value of F is possible

$$\frac{d}{dt} \hat{F} = \frac{\partial \hat{F}}{\partial t} + \frac{1}{i\hbar} \left[\hat{F}, \hat{H} \right]. \qquad \text{.......................[6]}$$

if $\frac{dF}{dt} = 0$, then $\hat{F}$ is called constant of motion. In this case, if $\hat{F}$ is an implicit function in t, then $\left[\hat{F}, \hat{H} \right] = 0$

Problem

For any dynamical variable $\hat{F}$, prove that

$$\frac{\partial \hat{F}}{\partial t} = -\left\{ \hat{F}, \hat{H} \right\}$$

where $\hat{H}$ H is the Hamiltonian operator.

Solution

$$\left[\hat{F},\hat{H}\right]\psi = i\hbar\left[\hat{F},\frac{\partial}{\partial t}\right]\psi$$

$$= i\hbar\left[\hat{F}\frac{\partial\psi}{\partial t} - \frac{\partial}{\partial t}(F\psi)\right]$$

$$= i\hbar\left[F\frac{\partial\psi}{\partial t} - F\frac{\partial\psi}{\partial t} - \psi\frac{\partial F}{\partial t}\right]$$

$$= -i\hbar\frac{\partial\hat{F}}{\partial t}\psi$$

$$\therefore \left[\hat{F},\hat{H}\right] = -i\hbar\frac{\partial\hat{F}}{\partial t}$$

$$\because \left[F,H\right] = i\hbar\left\{\hat{F},\hat{H}\right\}$$

$$\therefore \frac{\partial\hat{F}}{\partial t} = -\left\{\hat{F},\hat{H}\right\}$$

Solved Problems(A)

Problem (1):

Using Bohr-Sommerfeld quantization rule of the form $\oint P_i\, dq_i = n_i h$ solve the following problems:

(a) Determine the energy levels of a particle in a one-dimensional potential well with walls of infinite height at $x = 0$ and $x = a$.

(b) Quantize the motion of one-dimensional harmonic oscillator with

$$V(x) = \frac{1}{2} m \omega^2 x^2, w = \sqrt{k/m}$$

is the frequency of oscillation.

(c) A particle of mass m falls onto a horizontal plane and elastically bounces up. Quantize the particle's motion and determine the admissible heights H_n and calculate the energy of the system.

Solution:

(a) As the particle moves, its momentum P remains constant and is equal to P after the particle being reflected from the walls.

$$\oint P\,dx = 2P\int_0^a dx = nh$$

$$P_n = \frac{nh}{2a}$$

$$E_n = \frac{P_n^2}{2m} = \frac{n^2h^2}{8ma^2}$$

(b) The energy of the oscillator in fact is an integral of motion,

$$E = \frac{P^2}{2m} + \frac{m\,\omega^2 x^2}{2} = \frac{m\,\omega^2 A^2}{2}$$

Here A is the amplitude of oscillation.

$$\therefore P = \sqrt{m^2\omega^2\left(A^2 - x^2\right)}$$

Substituting $x = A\cos\varphi$ to get

$$\oint P\,dx = -\int m\,\omega A^2 \sin^2\varphi\,d\varphi$$

$$= m\,\omega A^2\pi = nh$$

Therefore the allowed amplitude and energies are given as:

$$A_n^2 = \frac{n\,h}{m\,\pi\,\omega}$$

$$E_n = \frac{m\,\omega^2}{2}A_n^2 = n\hbar\omega$$

(c) The particle's position z and its momentum P enter the total energy which is an integral of motion as:

$$E = \frac{P^2}{2m} + m\,g\,z = m\,g\,H$$

$$P = \pm\sqrt{2m\left(E - m\,g\,z\right)}$$

Using the quantization rule,

$$\oint P\,dz = 2\int_0^H \sqrt{2m\left(E - m\,g\,z\right)}\,dz$$
$$= n\,h$$

makes possibility to obtain H_n and E_n as:

$$H_n = \left\{\frac{3n\,h}{4m\sqrt{2g}}\right\}^{2/3} \quad ,E_n = \left\{\frac{3\sqrt{m}\,g\,n\,h}{4\sqrt{2}}\right\}^{2/3}$$

Problem (2):

(a) Let $\hat{A},\hat{B}$ and $\hat{C}$ be three operators. Express the commutator of the product $\hat{A}\,\hat{B}$ with $\hat{C}$ in terms of the commutator $\left[\hat{A},\hat{C}\right]$ and $\left[\hat{B},\hat{C}\right]$.

(b) Check hermiticty of the operator $\hat{P}_x = -2\hbar\frac{\partial}{\partial x}$.

(c) Find the operator that are hermitian conjugate to $\frac{\partial}{\partial x},\frac{\partial^n}{\partial x^n}$.

Solution:

(a)

$$\left[\hat{A}\,\hat{B},\hat{C}\right] = \left(\hat{A}\,\hat{B}\right)\hat{C} - \hat{C}\left(\hat{A}\,\hat{B}\right)$$
$$= \hat{A}\,\hat{B}\,\hat{C} - \hat{C}\,\hat{A}\,\hat{B} + \hat{A}\,\hat{C}\,\hat{B} - \hat{A}\,\hat{C}\,\hat{B}$$
$$= \hat{A}\left(\hat{B}\,\hat{C} - \hat{C}\,\hat{B}\right) + \left(\hat{A}\,\hat{C} - \hat{C}\,\hat{A}\right)\hat{B}$$

or in more compact form

$$\left[\hat{A}\,\hat{B},\hat{C}\right]=\hat{A}\left[\hat{B},\hat{C}\right]+\left[\hat{A},\hat{C}\right]\hat{B}$$

(b)

$$\int \Psi_2^*\left(-i\,\hbar\frac{\partial}{\partial x}\right)\Psi_1 dx=-2\hbar\int_{-\infty}^{\infty}\Psi_2^*\frac{\partial}{\partial x}\Psi_1 dx$$

$$=-2\hbar\left[\Psi_2^*\Psi_1\Big|_{-\infty}^{\infty}-\int_{-\infty}^{\infty}\Psi_1\frac{\partial}{\partial x}\Psi_2^* dx\right]$$

As before we have,

$$\int \Psi_2^*\left(-2\hbar\frac{\partial}{\partial x}\right)\Psi_1 dx=\int_{-\infty}^{\infty}\Psi_1\left(2\hbar\frac{\partial}{\partial x}\right)\Psi_2^* dx$$

$$=\int_{-\infty}^{\infty}\Psi_1\hat{A}\Psi_2^* dx$$

Then $\hat{P}_x$ is a hermitian operator.

(c) According to the definition of hermitian conjugate operator:

$$\int_{-\infty}^{\infty}\Psi_1^*\frac{d}{dx}\Psi_2 dx=\int_{-\infty}^{\infty}\Psi_2\left\{\left(\frac{d}{dx}\right)^{+}\Psi_1\right\}^* dx$$

Providing that $\int_{-\infty}^{\infty}|\Psi_1|^2 dx$ and $\int_{-\infty}^{\infty}|\Psi_2|^2 dx$ exist

and implies that Ψ_1 and Ψ_2 are zeros as $x\to\pm\infty$.

Integrating by parts to have:

$$\int_{-\infty}^{\infty}\Psi_1^*\frac{d}{dx}\Psi_2\,dx=\Psi_1^*\Psi_2\Big|_{-\infty}^{\infty}-\int_{-\infty}^{\infty}\Psi_2\frac{d}{dx}\Psi_1^*dx$$

$$=\int_{-\infty}^{\infty}\Psi_2\left(-\frac{d}{dx}\Psi_1\right)^*dx$$

Therefore

$$\left(\frac{d}{dx}\right)^+=-\frac{d}{dx}$$

In a similar manner one simply gets

$$\left(\frac{\partial^n}{\partial x^n}\right)^+=(-1)^n\frac{\partial^n}{\partial x^n}$$

Problem (3):

(a) Find the general solution of the one-dimensional time – dependent Schrödinger equation for free particle.

(b) Find the expectation values of position and momentum for a particle with a wave function

$$\Psi(x)=A\,e^{-\frac{x^2}{2a^2}+i\,k_0x}$$

then deduce $<\Delta x^2>$ and $<\Delta P^2>$.

Solution:

(a)

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi = i\,\hbar\frac{\partial \Psi(x,t)}{\partial t}$$

Let us make use of $\Psi(x,t)=U(x)\Phi(t)$ being considered as a particular solution as the variables may be separated

$$\frac{i\,\hbar}{\Phi}\frac{d\Phi}{dt} = -\frac{\hbar^2}{2mU}\frac{d^2U}{dx^2} = a$$

For $U(x)$ to be finite as $|x|\to\infty$ one must put $a>0$

Consider $k^2 = \frac{2m\,a}{\hbar^2}$, to get:

$$\Phi(t) = e^{\frac{i\hbar k^2}{2m}t} \qquad ,U(x) = e^{ikx}$$

where k is a real number. The general solution is:

$$\Psi(x,t) = \int_{-\infty}^{\infty} C(k)\,e^{ikx - i\hbar^2 t/2m}\,dk$$

(b)

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\Psi|^2\,dx = |A|^2 \int_{-\infty}^{\infty} x\,e^{-x^2/a^2}\,dx = 0,$$

$$<P>=\int_{-\infty}^{\infty}\Psi^*\left(-i\hbar\frac{\partial\Psi}{\partial x}\right)dx=\hbar k_0$$

Since $<x>=0$

$\therefore <\Delta x>=x-<x>=x$

$$<\Delta x^2>=\int_{-\infty}^{\infty}x^2|\Psi|^2dx=|A|^2\int_{-\infty}^{\infty}x^2e^{-x^2/a^2}dx$$

$$=\frac{|A|^2}{2}\sqrt{\pi}\,a^3$$

Normalizing the wave function to get:

$$|A|^2=(\pi a)^{-1/2}$$

Having:

$$<\Delta x^2><\Delta P^2>=\frac{\hbar^2}{4}$$

$$\therefore <\Delta P^2>=\frac{\hbar^2}{2a^2}$$

Problem (4):

Show that Newton's fundamental equation of classical dynamics:

$$\frac{dP}{dt}=F \quad \text{..[1]}$$

with P the momentum of the particle and F is the force acting upon the particle, still holds for the space

average (expectation values) of the corresponding operators in quantum mechanics.

Solution

If the force F derives from a potential, $F = -\nabla V$, and momentum is replaced by the operator $-i\hbar\nabla$ then the two space average in equation (1) are defined by:

$$P = \int \Psi^*(-i\hbar\nabla)\Psi d\Omega \text{ .... [2]}$$

$$F = -\int \Psi^*(\nabla V)\Psi d\Omega \text{ .... [3]}$$

Our task then is to prove that (1) is valid for the integrals (2), (3) if Ψ and Ψ^* satisfy the Schrödinger equations,

$$+i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \text{ .... [4]}$$

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi^* + V\Psi^* \text{ .... [5]}$$

We start proof with the time derivative of equation (2)

$$\dot{P} = \frac{\partial P}{\partial t} = -i\hbar\int \dot{\Psi}^*\nabla\Psi + \Psi^*\nabla\dot{\Psi} d\Omega$$

$$= -i\hbar\int\left(\dot{\Psi}^*\nabla\Psi - \dot{\Psi}\nabla\Psi^*\right)d\Omega$$

where the surface contribution of the particle integration in the last term vanishes and has been omitted.

Replacing Ψ^* and Ψ according to (4) and (5) we may proceed to,

$$\dot{P} = -\frac{\hbar^2}{2m}\int\left(\nabla^2\Psi^*\nabla\Psi + \nabla^2\Psi\nabla\Psi^*\right)d\Omega + \int\left(\Psi^* V\ \nabla\Psi + V\ \Psi\nabla\Psi^*\right)d\Omega \quad .[6]$$

A partial integration,

$$\int\nabla^2\Psi^*\nabla\Psi\, d\Omega = -\int\nabla\Psi^*\nabla^2\Psi\, d\Omega$$

Shows that the two terms of the first integral cancel each other out.

In the other hand the integral of equation (6) we perform a partial integration in the last term

$$\dot{P} = \int\Psi^*\left\{V\ \nabla\Psi - \nabla\left(V\ \Psi\right)\right\}d\Omega$$

Making use of

$$\nabla\left(V\ \Psi\right) = V\ \nabla\Psi + \Psi\nabla V$$

We finally arrive at

$$\dot{P} = -\int\Psi^*\left(\nabla V\right)\Psi\, d\Omega = F$$

as was to be proved.

Solved Problem (B)

Problem (1):

Determine if the operator $\left(\frac{\partial}{\partial x}\right)$ is hermitian or not.

Solution:

For hermitian operator $\hat{A}$, It must be hold that

$$\int \Psi_1 \hat{A}^* \Psi_2^* d\tau = \int \Psi_2^* \hat{A} \Psi_1 d\tau$$

In this case, we have

$$\int \Psi_2^* \hat{A} \Psi_1 d\tau = \int_{-\infty}^{\infty} \Psi_2^* \frac{\partial}{\partial x} \Psi_1 dx$$

$$= \Psi_2^* \Psi_1 \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi_1 \frac{\partial}{\partial x} \Psi_2^* dx$$

The 1[st] term vanishes, since $\Psi \to 0$ as $x \to \pm\infty$, and it must be finite or bounded. Then,

$$\int \Psi_2^* \frac{\partial}{\partial x} \Psi_1 dx = \int_{-\infty}^{\infty} \Psi_1 \left(-\frac{\partial}{\partial x}\right) \Psi_2^* dx$$

But $\frac{\partial}{\partial x}$ is a real operator $-\frac{\partial}{\partial x} \neq \hat{A}^*$, and then the operator $\frac{\partial}{\partial x}$ is not hermitian.

Problem (2):

Also for the operator $\hat{P}_x = -i\hbar\dfrac{\partial}{\partial x}$.

Solution:

$$\int \Psi_2^* \left(-i\hbar\frac{\partial}{\partial x}\right)\Psi_1 dx = -i\hbar\int_{-\infty}^{\infty}\Psi_2^*\Psi_1' dx$$

$$= -i\hbar\left[\Psi_2^*\Psi_1\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty}\Psi_1\frac{\partial}{\partial x}\Psi_2^* dx\right]$$

$$= +i\hbar\int_{-\infty}^{\infty}\Psi_1\frac{\partial}{\partial x}\Psi_2^* dx$$

As before,

$$\int \Psi_2^* \left(-i\hbar\frac{\partial}{\partial x}\right)\Psi_1 dx = \int_{-\infty}^{\infty}\Psi_1\left(i\hbar\frac{\partial}{\partial x}\right)\Psi_2^* dx$$

$$\therefore \int \Psi_2^* \hat{P}_x \Psi_1 dx = \int_{-\infty}^{\infty}\Psi_1 \hat{P}^* \Psi_2^* dx$$

Then $\hat{P}_x$ is a hermitian operator.

Problem (3):

Find $\left(\dfrac{\partial}{\partial t}P_x\right)$ for the function whose

Hamiltonian $H = \dfrac{P_x^2}{2m} + V(x)$.

Solution:

we know that,

$$\frac{d}{dt}P_x = \frac{\partial}{\partial t}P_x + \frac{1}{i\hbar}[P_x, H]$$

The 1^{st} term vanishes. Then,

$$\frac{d}{dt}P_x = \frac{1}{i\hbar}[P_x, H] \quad \text{....................................[1]}$$

Or,

$$\frac{d}{dt}P_x = \frac{1}{i\hbar}(P_x H - H P_x)$$

But,

$$(P_x H - H P_x)\Psi = \left[\frac{P_x^{\,3}}{2m} + P_x V(x)\Psi - \frac{P_x^{\,3}}{2m}\Psi - V(x)P_x\Psi\right]$$

$$= -i\hbar\left[\frac{\partial}{\partial x}V_x\,\Psi - V_x\frac{\partial\Psi}{\partial x}\right]$$

$$= -i\hbar\frac{\partial V_x}{\partial x}\cdot\Psi$$

From (1)

$$\therefore [P_x, H] \equiv -i\hbar\frac{\partial V_x}{\partial x}$$

$$\therefore \frac{d}{dt}\hat{P}_x \equiv \frac{1}{i\hbar}\left(-i\hbar\frac{\partial V_x}{\partial x}\right) = -\frac{\partial V_x}{\partial x}$$

Problem (3):

Prove that $\frac{d}{dt}\hat{x} \equiv \left(\frac{\hat{P}_x}{m}\right)$, for the function whose Hamiltonian,

$$H \equiv \frac{P_x^{\,2}}{2m} + V(x)$$

Solution:

$$\frac{d}{dt}\hat{x} = \frac{\partial \hat{x}}{\partial t} + \frac{1}{i\hbar}\left[\hat{x}, \hat{H}\right] = \frac{1}{i\hbar}[x, H] \text{ .....[1]}$$

As,

$$\left[\hat{x}, \hat{H}\right]\Psi = \left(\hat{x}\hat{H} - \hat{H}\hat{x}\right)\Psi$$

$$= x\,H\,\Psi - H\,x\,\Psi$$

$$= x\left[\frac{P_x^{\,2}}{2m} + V_x\right]\Psi - \left[\frac{P_x^{\,2}}{2m} + V_x\right]x\,\Psi$$

$$= x\,\frac{P_x^{\,2}}{2m}\Psi + x\,V_x\,\Psi - \frac{P_x^{\,2}}{2m}x\,\Psi - V_x\,x\,\Psi$$

$$\therefore [x, H]\Psi = \frac{x}{2m}(i\hbar)^2\frac{\partial^2\Psi}{\partial x^2} - \frac{(i\hbar)^2}{2m}\frac{\partial^2}{\partial x^2}x\,\Psi$$

$$= \frac{(i\hbar)^2}{2m}\left[x\,\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2}{\partial x^2}x\,\Psi\right]$$

But,

$$\frac{\partial^2}{\partial x^2} x\,\Psi = \frac{\partial}{\partial x}\left[x\frac{\partial\Psi}{\partial x} + \Psi\right] = x\frac{\partial^2\Psi}{\partial x^2} + 2\frac{\partial\Psi}{\partial x}$$

Then from (1),

$$[x, H]\Psi = -\frac{(i\hbar)^2}{2m}\cdot 2\cdot\frac{\partial}{\partial x}\Psi$$

$$\therefore \frac{d}{dt}\hat{x} \equiv \frac{1}{i\hbar}\left[-\frac{(i\hbar)^2}{m}\frac{\partial}{\partial x}\right] = \frac{P_x}{m}$$

Problem (4):

(i) Prove that $\frac{d}{dt}\left(\hat{r}\cdot\hat{P}\right) \equiv 2\hat{T} - r\,\text{grad}\,V(r)$ where

$\hat{T}$ is the K.E. operator whose hamiltonian is

$$H \equiv \frac{P_x^{\,2}}{2m} + V(x)$$

(ii) Also prove that $m\frac{d^2\hat{x}}{dt^2} = -\frac{\partial}{\partial x}V_x$.

Solution:

(i) $\because \frac{d}{dt}\left(\hat{r}\cdot\hat{P}\right) = \frac{d}{dt}\left(x\,P_x + y\,P_y + z\,P_z\right)$

But,

$$\frac{d}{dt}x\,P_x = x\frac{d}{dt}\hat{P}_x + P_x\frac{d}{dt}\hat{x}$$

$$= x\left(-\frac{\partial V}{\partial x}\right) + P_x\cdot\frac{P_x}{m} = \frac{P_x^{\,2}}{m} - x\frac{\partial V}{\partial x}$$

$$\therefore \frac{d}{dt}\left(\hat{r}\cdot\hat{P}\right)=\frac{P_x^{\,2}}{m}+\frac{P_y^{\,2}}{m}+\frac{P_z^{\,2}}{m}$$

$$-\left(x\,\frac{\partial V}{\partial x}+y\,\frac{\partial V}{\partial y}+z\,\frac{\partial V}{\partial z}\right)$$

$$=2\hat{T}-r\,\text{grad}\,V\left(r\right)$$

(ii) $$\frac{d^2}{dt^2}x=\frac{d}{dt}\cdot\frac{d}{dt}x$$

$$=\frac{d}{dt}\left(\frac{P_x}{m}\right)=\frac{1}{i\,\hbar}\left[\frac{P_x}{m},H\right]$$

$$=\frac{1}{i\,\hbar}\left[\frac{P_x}{m}\left(\frac{P_x^{\,2}}{2m}+V\right)-\left(\frac{P_x^{\,2}}{2m}+V\right)\frac{P_x}{m}\right]$$

$$\therefore\left(\frac{d^2}{dt^2}x\right)\Psi=\frac{1}{i\,\hbar}\left[\frac{P_x^{\,3}}{2m}\Psi+\frac{P_x}{m}V\,\Psi-\frac{P_x^{\,3}}{2m}\Psi-V\,\frac{P_x}{m}\Psi\right].$$

$$=\frac{1}{i\,\hbar}\frac{(i\,\hbar)}{m}\left[\frac{\partial}{\partial x}V\,\Psi-V\,\frac{\partial\Psi}{\partial x}\right]=-\frac{1}{m}\frac{\partial V}{\partial x}\Psi$$

$$\therefore m\,\frac{d^2x}{dt^2}=-\frac{\partial V}{\partial x}$$

Problem (3):

Find the mean value of $\hat{x},\hat{P}_x$ for the function

$$\Psi=\sqrt{2/a}\,\sin\left(\frac{n\,\pi}{a}x\right)$$

Solution:

$$<x>=\int_0^a \Psi^* x\,\Psi\,dx$$

$$=\int_0^a x\,\Psi^2\,dx$$

$$=\frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)dx$$

$$=\frac{2}{a}\int_0^a \frac{1}{2}x\left(1-\cos\left(\frac{n\pi}{a}x\right)\right)dx$$

$$=\frac{1}{a}\left[\frac{a^2}{2}-\int_0^a x\cos\left(\frac{n\pi}{a}x\right)dx\right]$$

$$=\frac{1}{a}\left[\frac{a^2}{2}-\left\{\frac{ax}{2n\pi}\sin\left(\frac{n\pi}{a}x\right)\right\}_0^a+\frac{a}{2n\pi}\int_0^a\sin\left(\frac{n\pi}{a}x\right)dx\right]$$

$$=\frac{1}{a}\left[\frac{a^2}{2}-0-\frac{a^2}{(2n\pi)^2}\left[\cos\left(\frac{n\pi}{a}x\right)\right]_0^a\right]$$

$$\therefore <x>=a/2$$

V

$V=\infty$ | $\Psi=0$ | $V=0$ | Ψ | $V=\infty$ | $\Psi=0$

0 well a x

$$< P_x >= \int_0^a \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi \, dx$$

$$= -i\hbar \frac{2}{a} \int_0^a \sin\left(\frac{n\pi}{a} x \right) \frac{\partial}{\partial x} \left(\sin\left(\frac{n\pi}{a} x \right) \right) dx$$

$$= -\frac{2\hbar n\pi}{a^2} \cdot \frac{1}{2} \int_0^a \sin\left(\frac{2n\pi}{a} x \right) dx$$

$$= \frac{i\hbar n\pi}{a^2} \cdot \frac{a}{2n\pi} \left[\cos\left(\frac{2n\pi}{a} x \right) \right]_0^a$$

$$= Zero$$

Problem (6):

Determine the energy levels and the normalized wave functions of a particle in a "*potential well*". The potential energy V of the particle is,

$V = \infty$ for $x < 0$ and $x > a$

$V = 0$ fro $0 < x < a$

Solution:

$$E_n = \frac{n^2 \hbar^3 \pi^2}{2m a^2} \quad ; \Psi_n = \sqrt{2/a} \sin\left(\frac{n\pi}{a} x \right)$$

Solved Problems (C)

Problem (1):

Consider a particle subjected to a time-independent potential $V(r)$.

(a) Assume that a state of the particle is described by a wave function of the form $\Psi(r,t)=\Phi(r)\mathrm{X}(t)$ Show that $\mathrm{X}(t)=e^{-i\omega t}$ (A is constant) and that $\Phi(r)$ must satisfy the equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Phi(r)+V(r)\Phi(r)=\hbar\omega\Phi(r).[1]$$

where m is the mass of the particle.

(b) Prove that the solutions of the Schrödinger equation of part (a) lead to a time-independent probability density.

Solution:

(a) We substitute $\Psi(r,t)=\Phi(r)\mathrm{X}(t)$ in the Schrödinger equation:

$$i\hbar\Phi(r)\frac{d\mathrm{X}(t)}{dt} = \mathrm{X}(t)\left[-\frac{\hbar^2}{2m}\nabla^2\Phi(r)\right]+\mathrm{X}(t)V(r)\Phi(r) \quad [2]$$

In the regions in which the wave function $\Psi(r,t)$ does not vanish, we divide both sides of (2) by $\Phi(r)\mathrm{X}(t)$; so we obtain,

$$\frac{i\hbar}{\mathrm{X}(t)}\frac{d\mathrm{X}(t)}{dt}=\frac{1}{\Phi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2\Phi(r)\right]+V(r) \quad [3]$$

The left hand side of (3) is a function of t only, and does not depend on r. On the other hand, the right-hand side is a function of r only. Therefore, both sides of (3) depend neither on r nor on t, and are thus constants that we will set equal to $\hbar\omega$ for convenience. Hence,

$$i\hbar\frac{1}{\mathrm{X}(t)}\frac{d\mathrm{X}(t)}{dt}=i\hbar\frac{d\left[\ln\mathrm{X}(t)\right]}{dt}=\hbar\omega \quad \text{.........}[4]$$

Therefore,

$$\begin{aligned}&\ln\mathrm{X}(t)=-\int i\,\omega dt=i\,\omega t+C\\&\Rightarrow\mathrm{X}(t)=A\,e^{-i\,\omega t}\end{aligned} \quad \text{...............}[5]$$

Where A is constant. Substituting in (3), we see that $\Phi(r)$ must satisfy the equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Phi(r)+V(r)\Phi(r)=\hbar\omega\Phi(r) \quad \text{........}[6]$$

(b) For a function of the form
$\Psi(r,t) = \Phi(r)e^{-i\omega t}$, the probability density is by definition,

$$P(r,t) = |\Psi(r,t)|^2 = \left[\Phi(r)e^{-i\omega t}\right]\left[\Phi(r)e^{-i\omega t}\right]^*$$

$$= \Phi(r)e^{-i\omega t}\Phi^*(r)e^{-i\omega t}$$

$$\therefore P(r,t) = |\Phi(r)|^2 \qquad [7]$$

We see that the probability density does not depend on time. This is why this kind of solution is called "*Stationary*".

Problem (2):

Consider a particle described by a wave function $\Psi(r,t)$. Calculate the time-derivative $\frac{\partial P(r,t)}{\partial t}$, where $P(r,t)$ is the probability density, and show that the continuity equation

$$\frac{\partial P(r,t)}{\partial t} + \nabla \cdot J(r,t) = 0$$

is valid, where $J(r,t)$ is the probability current, equal to $\frac{1}{m}\mathrm{Re}\left[\Psi^*\left(\frac{\hbar}{i}\nabla\Psi\right)\right]$.

Solution:

Using the Schrödinger equation,

$$-i\hbar\frac{\partial\Psi(r,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t)+V(r,t)\Psi(r,t) \quad [1]$$

Assuming $V(x)$ is real, the conjugate expression is

$$-i\hbar\frac{\partial\Psi^*(r,t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\Psi^*(r,t)+V(r,t)\Psi^*(r,t)$$

According to the definition of

$P(r,t)P(r,t)=\Psi(r,t)\Psi^*(r,t)$; hence,

$$\frac{\partial P(r,t)}{\partial t}=\frac{\partial\Psi^*(r,t)}{\partial t}\Psi(r,t)+\Psi^*(r,t)\frac{\partial\Psi(r,t)}{\partial t} \quad [2]$$

Using (1) and its conjugate, we arrive at

$$\frac{\partial P(r,t)}{\partial t}=\left[\frac{\hbar}{2mi}\Psi^*(r,t)\right]\Psi(r,t)-\frac{1}{i\hbar}V(r,t)\Psi(r,t)$$

$$-\Psi^*(r,t)\left[\frac{\hbar}{2mi}\nabla^2\Psi(r,t)\right]+\frac{1}{i\hbar}\Psi^*(r,t)V(r,t)$$

$$\frac{\partial P(r,t)}{\partial t}=-\frac{\hbar}{2mi}\left[\Psi^*(r,t)\nabla^2\Psi(r,t)-\Psi(r,t)\nabla^2\Psi^*(r,t)\right]$$

....[3]

We set

$$J(r,t)=\frac{1}{m}\mathrm{Re}\left[\Psi^*\left(\frac{\hbar}{i}\nabla\Psi\right)\right]$$
$$=\frac{\hbar}{2mi}\left[\Psi^*(r,t)\nabla\Psi(r,t)-\Psi(r,t)\nabla\Psi^*(r,t)\right] \quad [4]$$

Using the theorem

$$\nabla\cdot(U A)=(\nabla U)\cdot A+U(\nabla\cdot A)$$

We have,

$$\nabla\cdot J(r,t)=\frac{\hbar}{2m i}\left[(\nabla\Psi^*)\cdot(\nabla\Psi)+\Psi^*(\nabla^2\Psi)\right.$$
$$\left.-(\nabla\Psi)\cdot(\nabla\Psi^*)-\Psi(\nabla^2\Psi^*)\right]$$

$$\therefore\nabla\cdot J(r,t)=\frac{\hbar}{2m i}\left[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\right]\text{.......[5]}$$

So

$$\frac{\partial P(r,t)}{\partial t}+\nabla\cdot J(r,t)=0\text{ ....[6]}$$

Problem (3):

Consider a particle of mass m held in a one-dimensional potential $V(x)$. Suppose that in some region $V(x)$ is a constant, $V(x)=V$. For this region, find the stationary states of the particle when,

(a) $E>V$ (b) $E<V$ (c) $E=V$,

where E is the energy of the particle.

Solution:

(a) The stationary states are the solutions of,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Phi(x)}{\partial x^2}+V\,\Phi(x)=E\,\Phi(x)\text{ ......[1]}$$

for $E > V$, we introduce the positive constant k defined by:

$$k^2 = \frac{2m}{\hbar^2}(E - V)$$

So that,

$$\frac{\partial^2 \Phi(x)}{\partial x^2} + k^2 \Phi(x) = 0 \quad \text{......................... [2]}$$

The solution of this equation can be written in the form

$$\Phi(x) = A e^{ikx} + A' e^{-ikx} \quad \text{........................ [3]}$$

Where A and A' are arbitrary complex constants.

(b) We introduce the positive constant p defined by

$$p^2 = \frac{2m}{\hbar^2}(V - E)$$

So (1) can be written as,

$$\frac{\partial^2 \Phi(x)}{\partial x^2} - p^2 \Phi(x) = 0 \quad \text{......................... [4]}$$

The general solution of (4) is,

$$\Phi(x) = B e^{px} + B' e^{-px} \quad \text{........................ [5]}$$

B and B' are arbitrary complex constants.

(c) When $E = V$ we have

$$\frac{\partial^2 \Phi(x)}{\partial x^2} = 0$$

So is a linear function of x ,

$$\Phi(x) = C\,x + C' \text{ ....[6]}$$

where C and C' are complex constants.

Problem (4):

Consider a particle of mass m confined in an infinite one-dimensional potential well of width a:

$$V(x) = \begin{cases} 0 & -a/2 \le x \le a/2 \\ \infty & \text{oherwise} \end{cases} \text{ ....[1]}$$

Find the eigenstate of the Hamiltonian (i.e., the stationary states) and the corresponding eigen energies.

Solution:

For $x > a/2$ and $x < -a/2$ the potential is infinite, so there is no possibility of finding the particle outside the well. This means that,

$$\Psi(x > a/2) = 0 \quad , \Psi(x < a/2) = 0 \text{ .....[2]}$$

Since the wave function must be continuous, we also have, $\Psi(a/2) = \Psi(-a/2) = 0$ For $-a/2 \le x \le a/2$ the potential is constant, $V(x) = 0$; therefore we can rely

on the results of problem (3). We distinguish between three possibilities concerning the energy E.

As in problem (3), part (a), for $E > 0$ we define the positive constant k, $\hbar^2 k^2/2m = E$; so we obtain $\Phi(x) = A e^{ikx} + A' e^{-ikx}$. Imposing the continuous conditions, we arrive at

$$A e^{ika/2} + A' e^{-ika/2} = 0, \quad [3I]$$

$$A e^{-ika/2} + A' e^{ika/2} = 0 \quad [3II]$$

Multiplying (3I) by $e^{ika/2}$ we obtain $A' = -A e^{ika}$.
Substituting A' into (3II) yields,

$$A e^{-ika/2} - A e^{ika/2} e^{ika} = 0 \quad [4]$$

Multiplying (4) by $e^{-ika/2}$ and dividing by A [if $A = 0$ then $\Psi(x) = 0$] we obtain $e^{-ika} - e^{ika} = 0$. Using the relation $e^{i\alpha} = \cos\alpha + i\sin\alpha$ we have $-2i\sin(ka) = 0$. The last relation is valid only if $ka = n\pi$, where n is an integer. Also, since k must be positive, n must also be positive. We see that the possible positive eigen energies of the particle are

$$E_n = \frac{\hbar^2 k_n}{2m} = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 = \frac{\pi^2\hbar^2 n^2}{2ma^2} \text{.......[5]}$$

The corresponding eigenfunctions are

$$\Psi(x) = A e^{ikx} - A e^{ika} e^{-ikx} = A\left[e^{in\pi x/a} - e^{in\pi(a-x)/a}\right]$$

$$= A e^{in\pi/2}\left[e^{in\pi(x/a-1/2)} - e^{-in\pi(x/a-1/2)}\right]$$

$$\Psi_n = C\sin\left[n\pi\left(\frac{x}{a}-\frac{1}{2}\right)\right] \quad (n=1,2,\cdots) \text{...[6]}$$

where C is a normalization constant obtained by

$$\frac{1}{C^2} = \int_{-a/2}^{a/2} \sin^2\left[n\pi\left(\frac{x}{a}-\frac{1}{2}\right)\right]dx \text{ ....[7]}$$

defining $y = \left(\frac{x}{a}-\frac{1}{2}\right)$ and $dy = \frac{dx}{a}$,(7) becomes

$$\frac{1}{C^2} = a\int_{-1}^{0}\sin^2(n\pi y)dy = \frac{a}{2}\int_{-1}^{0}\left[1-\cos(2n\pi y)\right]dy$$

$$\frac{1}{C^2} = \frac{a}{2}\left[y - \frac{\sin(2\pi n y)}{2\pi n}\right]_{-1}^{0} = \frac{a}{2} \text{ ....[8]}$$

therefore, $C = \sqrt{a/2}$. Finally,

$$\Psi_n(x) = \sqrt{\frac{2}{a}}\sin\left[n\pi\left(\frac{x}{a}-\frac{1}{2}\right)\right] \text{ ....[9]}$$

consider now the case when $E < 0$.As in problem (3) part (b), we introduce the positive constant

$p, \hbar^2 p^2/2m = -E$. Stationary states should be of the form $\Psi(x) = B\,e^{px} + B'e^{-px}$. Imposing the boundary conditions, we obtain

$$B\,e^{px/2} + B'e^{-px/2} = 0 \quad \text{.......................... [10I]}$$

$$B\,e^{-px/2} + B'e^{px/2} = 0 \quad \text{.......................... [10II]}$$

Multiplying (10I) by $e^{px/2}$ yields $B' = -B\,e^{pa}$, so $B\,e^{-pa/2} - B\,e^{pa}e^{pa/2} = 0$. Multiplying by $e^{pa/2}$ and dividing by B, we obtain $1 - e^{2pa} = 0$. Therefore, $2p\,a = 0$. Since p must be positive, there are no states with corresponding negative energy.

Finally, we consider the case when $E = 0$. According to problem (3) part (c), we have $\Psi(x) = C\,x + C'$.

Imposing the boundary conditions yields

$$C\frac{a}{2} + C' = 0 \qquad , -C\frac{a}{2} + C' = 0 \quad \text{................[11]}$$

Solving these equations yields $C = C' = 0$, so the conclusion is that no possible state with $E = 0$.

Chapter (4)
Application of schrodinger equation



1. Particle in a Box:

Consider a free particle in a one- dimensional box. The particle has a mass m and is restricted to move in a straight line along the x -axis. The range of the particle is $0 < x < a$. The particle is reflected back whenever it reaches the end of the range. The general equation is,

$$\nabla^2\Psi + \left(\frac{2m}{\hbar^2}\right)(E - V)\Psi = 0 \text{ ....[1]}$$

For a free particle $V = 0$ for $0 < x < a$.

Also the wave function Ψ vanishes at $x = 0$ and $x = a$. For one-dimension, only the modified equation is given by,

$$\frac{\partial\Psi^2}{\partial x^2} + \left(\frac{2m}{\hbar^2}\right)E\,\Psi = 0 \text{ ....[2]}$$

$$\frac{\partial^2\Psi}{\partial x^2} + \left(\frac{8\pi^2 m\,E}{h^2}\right)\Psi = 0$$

Taking $\frac{8\pi^2 m\,E}{h^2} = k^2$

$$E = \frac{k^2 h^2}{8\pi^2 m}$$

$$\therefore \frac{\partial^2\Psi}{\partial x^2} + k^2\Psi = 0 \text{ ....[3]}$$

The general solution for equation (3) is given by:

$$\Psi(x) = A \sin k x + B \cos k x \quad \text{................[4]}$$

According to the boundary condition,

$$\Psi = 0 \text{ at } x = 0$$

Therefore from equation (4), B must be zero. But we cannot take A to be zero because it does not yield any solution. Hence $\sin ka = 0$ or

$$k a = n \pi$$

$$k = \frac{n \pi}{a} \text{ where } n \equiv 1, 2, 3, \cdots$$

Hence the only permissible solution of the wave equation are,

$$\Psi(x) = A \sin\left(\frac{n \pi}{a}\right) x \quad \text{............................[5]}$$

The value of energy is given by:

$$E = \frac{k^2 h^2}{8 \pi^2 m} \quad \text{..[6]}$$

$$E_n = \frac{n^2 h^2 \pi^2}{8 \pi^2 m a^2} = \frac{n^2 h^2}{8 m a^2}$$

$$\therefore E_n = \frac{n^2 h^2}{8 m a^2} = \left(\frac{\pi^2 \hbar^2}{2m}\right) \frac{n^2}{a^2} \quad \text{.........................[7]}$$

It means E_n depends upon the value of n. Each value of E_n is called Eigen value of proper value. Each value of Ψ_n is called Eigen function.

According to the requirement of the wave function,

$$\int_0^a |\Psi_n(x)|^2 dx = A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

Or $$\frac{A^2 a}{2} = 1$$

Or $$A = \sqrt{\frac{2}{a}}$$

$$\therefore \Psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\right)x$$

For $n = 1,2,3$

$$\Psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right)x$$

$$\Psi_2(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}\right)x$$

$$\Psi_3(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}\right)x$$

Plotting graphically, the firs three functions are shown in Fig. 1

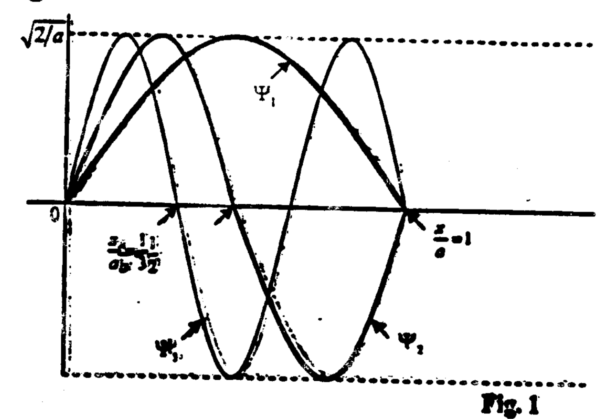


Fig. 1

Equation (7) represents that energy E_n of the particle is quantized.

Similarly for the momentum of the particle:

$$E_n = \frac{p_n^2}{2m}$$

Or $$p_n = (2mE_n)^{1/2} = \left(\frac{2m\,n^2h^2}{8ma^2}\right)^{1/2}$$

Or $$p_n = \frac{nh}{2a}$$

$$\therefore p_n \propto n$$

It means the momentum of the particle is also quantized. Further, for each value of E_n, there is a corresponding value of p_n.

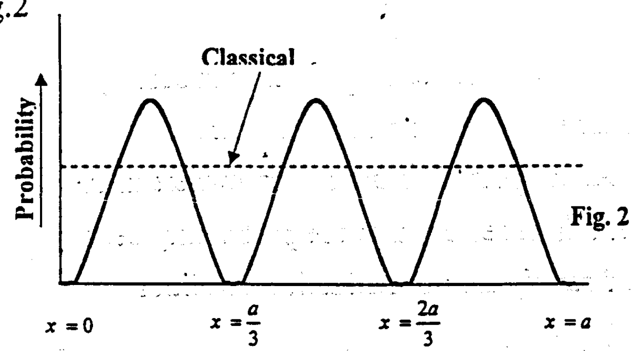
According to quantum mechanics the probability is given by,

$$|\Psi_n(x)|^2 dx = \frac{2}{a}\sin^2\left(\frac{n\pi x}{a}\right)dx$$

This is wave like function and for $n=3$,

$$|\Psi_3(x)|^2 dx = \frac{2}{a}\sin^2\left(\frac{3\pi x}{a}\right)dx$$

The graph between probability and x is shown in Fig.2



In the graph the doted line represents the constant probability according to classical mechanics. But the curve represents the probability variation with variation of x according to quantum mechanics. The probability is zero for values of,

$$x = 0\ , x = \frac{a}{3}\ , x = \frac{2a}{3} \text{ and } x = a$$

and so on.

Wave Function and probability Density

The basic postulate of quantum mechanics is that the quantity $\Psi\Psi^* dx\, dy\, dz$ is the *probability* that particle represented by the wave function $\Psi(x,y,z,t)$ is in the volume $dV = (dx\, dy\, dz)$ at the time t.

Ψ^* is the complex conjugate of Ψ. The probability density of the particle is:

$$P(t) = \Psi\Psi^* = |\Psi(x,y,z,t)|^2$$

The wave function Ψ is the probability amplitude for the position of the particle.

As the particle must be somewhere in the space, it is necessary that the probability density should satisfy the normalization condition

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi\Psi^* dx\, dy\, dz = 1 \text{ ....[1]}$$

Here $\Psi = \Psi_0 e^{-i\omega t}$ But $\omega = \frac{2\pi E}{h} = \frac{E}{\hbar}$

$$\text{Or } \Psi = \Psi_0 e^{\frac{-2i\omega E t}{h}} \text{ ....[2]}$$

$$\text{Or } \Psi = \Psi_0 e^{-iEt/\hbar} \text{ ....[3]}$$

The complex conjugate is,

$$\Psi^* = \Psi^*_0 e^{\frac{-2i\omega E t}{h}} \text{ ....[4]}$$

Or $\Psi^* = \Psi^*_0 e^{-iEt/\hbar}$ ....[5]

Substituting these values of Ψ and Ψ^* in equation (1),

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi_0 \Psi_0^* dx\, dy\, dz = 1 \quad \text{..........................[6]}$$

Thus for a wave function satisfying the time independent Schrödinger equation, the probability is also independent of time.

Therefore Ψ has the following limitations.

(1) The wave function Ψ besides being nonmalleable must be single valued as $P(t)$ can have only one value at a particular place at a particular time.

(2) Wave function Ψ and its partial derivation $\frac{d\Psi}{dx}, \frac{d\Psi}{dy}$ and $\frac{d\Psi}{dz}$ must be continuous every where.

(3) Ψ must be finite for all values of x, y and z.

2. Potential Step

The general Schrödinger equation is

$$\nabla^2\Psi + \left(\frac{2m}{\hbar^2}\right)(E - V)\Psi = 0 \quad \text{.........................[1]}$$

For one dimension only the modified equation is given by (particle constrained to move to along the x -axis).

$$\frac{\partial^2\Psi}{\partial x^2} + \left(\frac{2m}{\hbar^2}\right)(E - V)\Psi = 0 \quad \text{.........................[2]}$$

If the total energy of the particle has a fixed value E, the time dependent equation is given by,

$$\Psi(x,t) = \Psi_0 e^{-i\omega t} = \Psi_0 e^{-(i/\hbar)Et} \quad \text{....................[3]}$$

Therefore Ψ also satisfies the time-independent Schrödinger equation

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right)(E - V)\Psi = 0 \quad \text{.........................[4]}$$

The square potential step is shown in Fig. 3

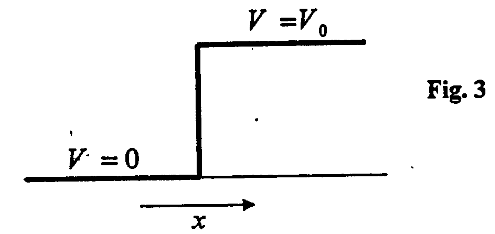


Fig. 3

Here

$$\left.\begin{array}{lll} V_n = 0 & \text{for} & x < 0 \\ V_n = V_0 & \text{for} & x > 0 \end{array}\right\} \quad \text{..........................[5]}$$

Therefore time independent Schrödinger equation

(1) For $x < 0$ is given by,

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right) E\,\Psi = 0$$

Taking $k_0^2 = \left(\frac{2mE}{\hbar^2}\right)$,

$$\therefore \frac{d^2\Psi}{dx^2} + k_0^2\Psi = 0 \quad \text{....................................[6]}$$

(2) For $x > 0, V_n = V_0$

$$\frac{d^2\Psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right)(E - V_0)\Psi = 0$$

Taking $k^2 = \left(\frac{2m}{\hbar^2}\right)(E - V_0)$,

$$\therefore \frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \quad \text{....................................[7]}$$

The solution of equations (6) and (7) are

$$\Psi = A e^{ik_0x} + Be^{-ik_0x} \quad (\text{for } x < 0) \text{.........[8]}$$

$$\Psi = C e^{ikx} + De^{-ikx} \quad (\text{for } x > 0) \text{..........[9]}$$

Here A, B, C and D are integration constants.

There is discontinuity of V at $x = 0$.

The Schrödinger equation changes discontinuity at $x = 0$.

The constant of integrations A, B, C and D must be so chosen that Ψ and its derivatives are continuous at this point. It means wave functions must be equal at $x = 0$.

From equations (8) and (9) when $x = 0$

$$\Psi = A + B \quad and \ \Psi = C + D$$

$$\therefore A + B = C + D \qquad [10]$$

When derivatives of equation (8) and (9) are made equal at $x = 0$, in that case

$$\frac{d\Psi}{dx} = k_0(A - B) \ and \ \frac{d\Psi}{dx} = k(C - D)$$

$$\therefore k_0(A - B) = k(C - D) \qquad [11]$$

$$A - B = \left(\frac{k}{k_0}\right)(C - D) \qquad [12]$$

From equations (10) and (12)

$$B = \left(\frac{k_0 - k}{k_0 + k}\right)A + \left(\frac{2k}{k_0 + k}\right)D \qquad [13]$$

$$, C = \left(\frac{2k_0}{k_0 + k}\right)A - \left(\frac{k_0 - k}{k_0 + k}\right)D \qquad [14]$$

Substituting the value B in equation (8) for $x < 0$

$$\Psi = Ae^{ik_0x} + \left[\left(\frac{k_0-k}{k_0+k}\right)A + \left(\frac{2k}{k_0+k}\right)D\right]e^{-ik_0x}$$

$$\Psi = A\left[e^{ik_0x} + \left(\frac{k_0-k}{k_0+k}\right)e^{-ik_0x}\right] + D\left[\left(\frac{2k}{k_0+k}\right)e^{-ik_0x}\right]$$

Taking

$$\left.\begin{aligned} e^{ik_0x} + \left(\frac{k_0-k}{k_0+k}\right)e^{-ik_0x} &= \Psi_1 \\ \text{and} \quad \left(\frac{k_0-k}{k_0+k}\right)e^{-ik_0x} &= \Psi_2 \end{aligned}\right] \text{for } x < 0$$

$$\Psi = A\Psi_1 + D\Psi_2 \text{ ....[15]}$$

Substituting the value C in equation (9) for $x > 0$

$$\Psi = \left[\left(\frac{2k_0}{k_0+k}\right)A - \left(\frac{k_0-k}{k_0+k}\right)D\right]e^{ikx} + De^{-ikx}$$

$$\Psi = A\left[\left(\frac{2k_0}{k_0+k}\right)e^{ikx}\right] + D\left[e^{-ikx} - \left(\frac{k_0-k}{k_0+k}\right)e^{-ik_0x}\right]$$

Taking

$$\left.\begin{aligned} \left(\frac{2k_0}{k_0+k}\right)e^{ikx} &= \Psi_1 \\ \text{and} \quad \left[e^{-ikx} - \left(\frac{k_0-k}{k_0+k}\right)e^{ikx}\right] &= \Psi_2 \end{aligned}\right] \text{for } x > 0$$

$$\Psi = A\Psi_1 + D\Psi_2 \text{ ....[16]}$$

The equations (15) and (16) are the same and conditions of continuity at $x = 0$ are satisfied by both

Ψ_1 and Ψ_2. Also another condition to be imposed upon the wave function is that Ψ must remain finite as $|x|$ becomes finite.

3. Particle in three Dimensional Box

Consider a particle enclosed in a three dimensional box of length a, breadth b, height c whose walls are rigid and hard. (Fig.6). The potential energy is assumed to be zero inside the box. As no force acts on the particle inside the box, therefore in this region

$$0 < x < a$$
$$0 < y < b$$
$$0 < z < c$$

The potential energy $V(x,y,z) = 0$ and for region outside the box, $V(x,y,z) = \infty$

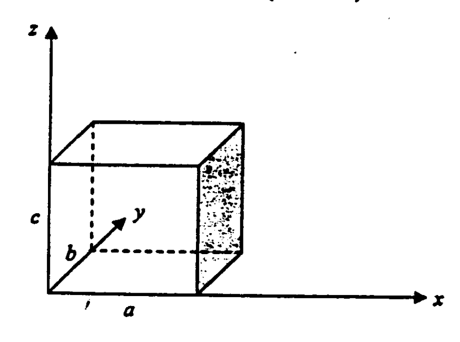


Fig. 6

The Schrödinger equation is

$$\nabla^2\Psi + \left(\frac{2m}{\hbar^2}\right)(E - V)\Psi = 0 \quad \text{.............................[1]}$$

For a particle inside the box, $V = 0$

$$\therefore \nabla^2\Psi + \left(\frac{2mE}{\hbar^2}\right)\Psi = 0 \quad \text{.......................[2]}$$

or $$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dx^2} + \left(\frac{2mE}{\hbar^2}\right)\Psi = 0 \quad \text{............[3]}$$

Applying the method of separation of variables, we get,

$$\Psi(x,y,z) = X(x)Y(y)Z(z) \quad \text{..................[4]}$$

It means wave function $\Psi(x,y,z)$ is equal to product of the function X, Y and Z.

Take the second derivatives and substituting their values in equation (3) we get,

$$YZ\frac{d^2X}{dx^2} + ZX\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + \left(\frac{2mE}{\hbar^2}\right)XYZ = 0 \quad [5]$$

Dividing by XYZ, we get,

$$\left(\frac{1}{X}\right)\frac{d^2X}{dx^2} + \left(\frac{1}{Y}\right)\frac{d^2Y}{dy^2} + \left(\frac{1}{Z}\right)\frac{d^2Z}{dz^2} + \left(\frac{2mE}{\hbar^2}\right) = 0 \quad ...[6]$$

For a particular value of kinetic energy, the term $\left(\frac{2mE}{\hbar^2}\right)$ has a constant value.

As velocity is a vector quantity and can be resolved into three components along the co-ordinate axes. Therefore kinetic energy E can be resolved into three components such that,

$$E_t = E_x + E_y + E_z \quad \text{.......................................[7]}$$

Substituting this value in equation (6) and rearranging,

$$\left[\left(\frac{1}{X}\right)\frac{d^2X}{dx^2}+\frac{2mE_x}{\hbar^2}\right]+\left[\left(\frac{1}{Y}\right)\frac{d^2Y}{dy^2}+\frac{2mE_y}{\hbar^2}\right]+\left[\left(\frac{1}{Z}\right)\frac{d^2Z}{dz^2}+\frac{2mE_z}{\hbar^2}\right]=0$$

This equation gives three independent equations which are as follows,

$$\frac{d^2X}{dx^2}+\left(\frac{2mE_x}{\hbar^2}\right)X=0 \quad \text{.................................[8]}$$

$$\frac{d^2Y}{dy^2}+\left(\frac{2mE_y}{\hbar^2}\right)Y=0 \quad \text{.................................[9]}$$

$$\frac{d^2Z}{dz^2}+\left(\frac{2mE_z}{\hbar^2}\right)Z=0 \quad \text{.................................[10]}$$

The boundary conditions applicable to the solution are

$$X=0 \quad \text{at } x=0,a$$

$$Y=0 \quad \text{at } y=0,b$$

$$Z=0 \quad \text{at } z=0,c$$

The general solution for X, Y and Z are,

$$X=X_0\sin\left[\left(\frac{2mE_x}{\hbar^2}\right)^{1/2}x+\varphi_x\right] \quad \text{..................[11]}$$

$$Y = Y_0 \sin\left[\left(\frac{2mE_y}{\hbar^2}\right)^{1/2} y + \varphi_y\right] \quad \text{[12]}$$

$$Z = Z_0 \sin\left[\left(\frac{2mE_z}{\hbar^2}\right)^{1/2} z + \varphi_z\right] \quad \text{[13]}$$

The boundary condition $X = 0, Y = 0, Z = 0$ are satisfied at $x = 0, y = 0, z = 0$ if we take

$$\varphi_x = 0,\ \varphi_y = 0 \text{ and } \varphi_z = 0$$

In order to satisfy the boundary condition

$$X = 0 \text{ at } x = a$$

$$Y = 0 \text{ at } y = b$$

and $$Z = 0 \text{ at } z = c$$

It is necessary that energies assume Eigen values given by

$$E_x = \frac{\pi^2\hbar^2 n_x^{\,2}}{2ma^2} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^{\,2}}{a^2}\right) \quad \text{[14]}$$

$$E_y = \frac{\pi^2\hbar^2 n_y^{\,2}}{2mb^2} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_y^{\,2}}{b^2}\right) \quad \text{[15]}$$

$$E_z = \frac{\pi^2\hbar^2 n_z^{\,2}}{2mc^2} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_z^{\,2}}{c^2}\right) \quad \text{[16]}$$

Here n_x, n_y and n_z are integers.

The total energy of the particle

$$E = E_x + E_y + E_z$$

$$E = \frac{\pi^2\hbar^2}{2m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \qquad \text{[17]}$$

Here

$$n_x = 1,2,3,\cdots \quad n_y = 1,2,3,\cdots \quad n_z = 1,2,3,\cdots$$

The wave function Ψ for a particle is obtained from equation (11), (12) with normalization over the volume of the box

$$\Psi = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \qquad \text{[18]}$$

Results:

(1) n_x, n_y and n_z are integers and are called quantum numbers. n_x, n_y and n_z have positive integral values.

(2) The lowest possible energy occurs when

$$n_x = n_y = n_z = 1$$

$$\therefore E_{111} = \frac{\pi^2\hbar^2}{2m}\left[\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right] \qquad \text{[19]}$$

(3) **Non-Degenerate Energy Levels**

For a particle contained in a cubical box of length l

$$E = \frac{\pi^2\hbar^2}{2ml^2}\left[n_x^2 + n_y^2 + n_z^2\right] \qquad \text{[20]}$$

The energy in the ground state is given by

$$E_{111} = \frac{3\pi^2\hbar^2}{2ml^2} \quad \text{..[21]}$$

In this case, no other state will have this energy. This state has only one wave function. Therefore the ground state and this energy level is said to be **Non-degenerate.**

(4) Degenerate Energy Levels

As for a particle in a cubical box the energy depends upon the sum of the square of the quantum numbers, the particles having same energy in an excited state can have different energy levels and different wave functions. Such states and energy levels are said to be degenerate.

Examples:

(1) For first excited state the possible values of quantum numbers are

n_x	n_y	n_z
2	1	1
1	2	1
1	1	2

Therefore there are three different energy states having same energy. The energy in this case

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2ml^2}$$

As the number of different wave functions in this case is 3, therefore the degree of degeneracy of energy level is said to be *three fold.*

(2) For second excited state

n_x	n_y	n_z
2	2	1
2	1	2
1	2	2

$$E_{221} = E_{212} = E_{122} = \frac{9\pi^2\hbar^2}{2ml^2}$$

It is *three fold* degenerate

(3) For $n_x = 2, n_y = 2, n_z = 2$

$$E_{222} = \frac{12\pi^2\hbar^2}{2ml^2}$$

It is *non degenerate*

Similarly degree of degeneracy for any energy level can be calculated.

4 Linear Harmonic Oscillator (One Dimensional)

Consider a particle of mass m vibrating along the x -axis and executing simple harmonic motion. The restoring force on the particle is F and is directed towards the mean position. F depends upon the displacement x .

$$\therefore F = -Kx \quad \text{.......................................[1]}$$

where K is force constant.

But $$F = m\frac{d^2x}{dt^2}$$

$$\therefore m\frac{d^2x}{dt^2} = -Kx \quad \text{.......................................[2]}$$

$$\text{or } m\frac{d^2x}{dt^2} + Kx = 0 \quad \text{.......................................[3]}$$

This is the general equation of SHM.

The general equation is,

$$\frac{d^2x}{dt^2} + \omega^2 x = 0 \quad \text{.......................................[4]}$$

Comparing equation (3) and (4)

$$\therefore \omega = \sqrt{\frac{K}{m}}$$

also $$K = m\omega^2$$

but $$\omega = 2\pi\nu$$

$$\therefore K = 4\pi^2 m \nu^2 \quad \text{...[5]}$$

Here ν is the frequency of oscillation and ω is the angular frequency.

The potential energy of the harmonic oscillator is given by,

$$V = -\int F\,dx$$

but

$$F = -Kx$$

$$V = \int Kx\,dx$$

$$\therefore V = \frac{1}{2}Kx^2 + C \quad \text{...[6]}$$

Here C is the constant of integration.

When the particle is in the mean position, x is zero and its potential energy is also zero. Therefore from equation (6)

$$0 = 0 + C \qquad \Rightarrow C = 0$$

Hence from equation (6)

$$\therefore V = \frac{1}{2}Kx^2 \quad \text{...[7]}$$

Substituting the value of $K = 4\pi^2 m\nu^2$ in equation (7) we get

$$V = 2\pi^2 m\nu^2 x^2 \quad \text{...[8]}$$

This is the potential energy of the harmonic oscillator.

If a is the amplitude, then the maximum potential energy of the harmonic oscillator is given by,

$$V = 2\pi^2 m\nu^2 a^2 \quad \text{.......................................[9]}$$

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\Psi = 0 \quad \text{..........................[10]}$$

represents Schrödinger equation.

Substituting the value of $V = \frac{1}{2}Kx^2$ in equation (10) we get,

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - \frac{1}{2}Kx^2\right]\Psi = 0 \quad \text{....................[11]}$$

Also

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}\left[E - 2\pi^2 m\nu^2 x^2\right]\Psi = 0$$

or

$$\frac{d^2\Psi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \frac{4\pi^2 m^2\nu^2 x^2}{\hbar^2}\right]\Psi = 0 \quad \text{.............[12]}$$

Taking $\lambda = \dfrac{2E}{\hbar(2\pi\nu)}$

Here λ is eigen value, a pure dimensionless quantity, where

$$\lambda_n = (2n+1)$$

and
$$\frac{2\pi m\nu}{\hbar} = \alpha^2$$

$$\alpha^2\lambda = \frac{2mE}{\hbar^2}$$

Substituting these values in equation (12)

$$\frac{d^2\Psi}{dx^2} + \left(\alpha^2\lambda - \alpha^4 x^2\right)\Psi = 0 \quad \text{.........................[13]}$$

Dividing by α^2

$$\frac{1}{\alpha^2}\frac{d^2\Psi}{dx^2} + \left(\lambda - \alpha^2 x^2\right)\Psi = 0 \quad \text{.........................[14]}$$

Taking new variable $\xi = \alpha x \qquad \Rightarrow \frac{d\xi}{dx} = \alpha$

where α is a constant.

$$\frac{d\Psi}{dx} = \frac{d\Psi}{d\xi}\frac{d\xi}{dx} = \alpha\frac{d\Psi}{d\xi} \quad \text{.........................[15]}$$

$$\frac{d^2\Psi}{dx^2} = \frac{d}{dx}\left(\frac{d\Psi}{dx}\right) = \frac{d}{d\xi}\left(\frac{d\Psi}{dx}\right)\frac{d\xi}{dx} = \frac{d}{d\xi}\left(\frac{d\Psi}{dx}\right)\alpha$$

Substituting $\frac{d\Psi}{dx} = \alpha\frac{d\Psi}{d\xi}$ in the above equation,

we get

$$\frac{d^2\Psi}{dx^2} = \frac{d}{d\xi}\left[\alpha^2\frac{d\Psi}{d\xi}\right] = \alpha^2\frac{d^2\Psi}{d\xi^2}$$

$$\therefore \frac{1}{\alpha^2}\frac{d^2\Psi}{dx^2} = \frac{d^2\Psi}{d\xi^2}$$

Substituting these values in equation (14)

$$\frac{d^2\Psi}{d\xi^2}+\left(\lambda-\xi^2\right)\Psi=0 \qquad [16]$$

Solution.

When $\xi^2>\lambda$, λ can be neglected in equation (16).

$$\therefore \frac{d^2\Psi}{d\xi^2}-\xi^2\Psi=0 \qquad [17]$$

Its general solution is

$$\Psi=e^{\pm\xi^2/2} \qquad [18]$$

There are two possible solutions

$$(i) \quad \Psi=e^{\xi^2/2}$$

and $$(ii) \quad \Psi=e^{-\xi^2/2} \qquad [19]$$

Since $|\Psi|^2$ is the probability of locating along x -axis, therefore it must decrease continuously to zero as x or ξ approaches $\pm\infty$.

Therefore, the first solution is not possible hence the second solution holds good.

Recursion Formula:

It is clear that equation (19) contains the term $e^{-\xi^2/2}$ as a factor.

The solution of equation (19) can be written as

$$\Psi = e^{-\xi^2/2}\phi(\xi) \text{ ....} [20]$$

Here $\phi(\xi)$ is a function of ξ and also therefore of x.

Differentiating equation (20) twice with respect of ξ we get,

$$\frac{d^2\Psi}{d\xi^2} = e^{-\xi^2/2}\left[\frac{d^2\phi}{d\xi^2} - 2\xi\frac{d\Psi}{d\xi} + (\xi^2 - 1)\phi\right] \text{......} [21]$$

Substituting the value of Ψ and $\frac{d^2\Psi}{d\xi^2}$ in equation (16) and simplifying we get,

$$\frac{d^2\phi}{d\xi^2} - 2\xi\frac{d\phi}{d\xi} + (\lambda - 1)\phi = \text{υ} \text{ ....} [22]$$

Now representing the solution of equation (22) in the form of power series of ξ

$$\phi(\xi) = \sum_{n=0}^{\infty} a_n\xi^n = a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3 + \cdots \text{ ..} [22\text{-a}]$$

Differentiating above equation *w.r.t.* ξ

$$\frac{d\phi}{d\xi} = \sum_{n=1}^{\infty} na_n\xi^{n-1} = a_1 + 2a_2\xi + 3a_3\xi^2 + \cdots$$

Differentiating further *w.r.t.* ξ we get,

$$\frac{d^2\phi}{d\xi^2} = \sum_{n=2}^{\infty} n(n-1)a_n\xi^{n-2} = 2a_2 + 6a_3\xi + 12a_4\xi^2 + \cdots$$

Substituting these values in equation (22) we get,

$$\sum_{n=2}^{\infty} n(n-1)a_n\xi^{n-2} - 2\sum_{n=1}^{\infty} na_n\xi^{n-1} + (\lambda+1)\sum_{n=0}^{\infty} a_n\xi^n = 0$$

$$\sum_{n=2}^{\infty} n(n-1)a_n\xi^{n-2} + (\lambda-2n-1)\sum_{n=0}^{\infty} a_n\xi^n = 0 \quad ..[23]$$

This equation is satisfied for all values of ξ, if the coefficients of each power of ξ vanishes separately [i.e. here for the first term n should be taken as $(n+2)$].

$$(n+2)(n+1)a_{n+2} + (\lambda-2n-1)a_n = 0$$

$$\therefore a_{n+2} = \frac{2n+1-\lambda}{(n+2)(n+1)}a_n \quad \text{.............................[24]}$$

This is known as *Recursion formula.*

Eigen Values of harmonic Oscillator:

In order to obtain a satisfactory wave function the series given in equation (22-a) should break off a finite number of terms. In equation (24) the term $(2n+1-\lambda)$ must be zero, so that the series break off after the nth i.e. the finite term.

$$(2n+1-\lambda) = 0 \Rightarrow \lambda = 2n+1 \quad \text{......................[25]}$$

Here λ is dimensionless Eigen value.

But $\lambda = \frac{2E}{\hbar(2\pi\nu)}$ ....[26]

$\therefore$ Equating (25) and (26)

$$2n+1 = \frac{2E}{\hbar(2\pi\nu)}$$

$$E = \left[n + \frac{1}{2}\right]\hbar(2\pi\nu)$$

$$E = \left[n + \frac{1}{2}\right]\hbar\omega$$

$$E = \left[n + \frac{1}{2}\right]h\nu \quad n = 0,1,2,3,\cdots \text{ ....[27]}$$

It means the energy of harmonic oscillator has discrete values depending upon the value of n. The difference in energies between two adjacent states is $h\nu$.

Zero Point Energy

The energy of the linear harmonic is given by the equation,

$$E_n = \left[n + \frac{1}{2}\right]h\nu$$

Even for $n = 0$

$$E_0 = \frac{1}{2}h\nu$$

It means even foe ground state the even for ground state the energy is not zero but it is $\frac{1}{2}h\nu$. Thus ground state energy $\frac{1}{2}h\nu$ is called zero point energy

In old mechanics:

$$E_n = nh\nu$$

but in wave mechanics:

$$E_n = \left[n + \frac{1}{2}\right]h\nu$$

The only differences is, that the energy levels are shifted by an amount $\frac{1}{2}h\nu$. The difference in energy in various energy levels however remains the same.

The pres of zero point energy has been found to be experimentally true.

Example:

A particle one-dimensional potential well $0 \le x \le a$ for which:

$$V = \begin{cases} \infty & x \le 0 \\ 0 & 0 \le x \le a \\ \infty & x \ge a \end{cases}$$

Solve the time – independent Schrödiger equation for this case.

Solution:

$V = 0$ Ψ_1 | $V = 0$ Ψ_2 | $V = 0$ Ψ_1

$V = 0$

Ψ_1

Chapter (5)

Angular momentum in polar coordinates

The theory of angular momentum plays an important role in quantum physics. This is only partly because angular momentum is a constant of the motion for many systems.

1. Orbital Angular Momentum Operates in Polar Coordinates

In three dimensional classical mechanics, the orbital angular momentum of a particle is defined as:

$$\bar{L} = \bar{r} \times \bar{P} \quad \text{..[1]}$$

where $\bar{r}$ and $\bar{P}$ represent respectively the position, and momentum of the particle. The Cartesian components of the vector $\bar{L}$ are:

$$\left.\begin{aligned} L_x &= yP_z - zP_y \\ L_y &= zP_x - xP_z \\ L_z &= xP_y - yP_x \end{aligned}\right\} \quad \text{..............................[2]}$$

where x, y, z and P_x, P_y, P_z are the components of the vector $\bar{r}$ and $\bar{P}$ respectively.

In order to obtain the quantal operator of the orbital angular momentum, we replace P_x, P_y, P_z with their quantal equivalents $\frac{\hbar}{i}D_x, \frac{\hbar}{i}D_y, \frac{\hbar}{i}D_z$.

Thus the operators for the orbital angular momentum components are,

$$\left.\begin{aligned} \hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{aligned}\right\} \text{.................[3]}$$

or in a compact notation as,

$$\hat{L}_\alpha = -\hbar\left(\beta D_\gamma - \gamma D_\beta\right)\cdot \varepsilon_{\alpha\beta\gamma}$$

where

$$\varepsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \text{if } \alpha,\beta,\gamma \text{ form an even permutation } x,y,z \\ -1 & \text{if } \alpha,\beta,\gamma \text{ form an odd permutation } x,y,z \\ 0 & \text{unless } \alpha,\beta,\gamma \text{ are } x,y,z \end{cases}$$

The square of the magnitude of the operator $\hat{L}$ is:

$$\hat{L}^2 = \hat{L}_x^{\ 2} + \hat{L}_y^{\ 2} + \hat{L}_z^{\ 2} \text{ ....[4]}$$

To represent the Cartesian components of the orbital angular momentum operator $\hat{L}$ in terms of spherical polar coordinates, we need to express the Cartesian differential operators D_x, D_y, D_z of terms of the polar differential operators D_r, D_θ, D_φ.

Having:

$$\left.\begin{aligned} x &= r\sin\theta\cos\varphi \\ y &= r\sin\theta\sin\varphi \\ z &= r\cos\theta \end{aligned}\right\} \text{..............................[5]}$$

one simply obtains

$$
\left.
\begin{aligned}
r &= \left[x^2+y^2+z^2\right]^{1/2} \\
\theta &= \arccos\left[z\Big/\left(x^2+y^2+z^2\right)^{1/2}\right] \\
\varphi &= \arccos\left[x\Big/\left(x^2+y^2+z^2\right)^{1/2}\right]
\end{aligned}
\right\} \text{......[6]}
$$

In spherical polar representation the Cartesian differential operators D_x, D_y, D_z then read,

$$
D_\mu = D_r D_\mu r + D_\theta D_\mu \theta + D_\varphi D_\mu \varphi \text{ ....[7]}
$$

where μ stands for x, y and z. Consequently one obtains

$$
\left.
\begin{aligned}
D_x &= \sin\theta\cos\varphi D_r + \frac{1}{r}\cos\theta\cos\varphi D_\theta - \frac{\sin\varphi}{r\sin\theta} D_\varphi \\
D_y &= \sin\theta\sin\varphi D_r + \frac{1}{r}\cos\theta\sin\varphi D_\theta + \frac{\cos\varphi}{r\sin\theta} D_\varphi \\
D_z &= \cos\theta D_r - \frac{1}{r}\sin\theta D_\varphi
\end{aligned}
\right\} \text{[8]}
$$

The orbital angular momentum components in spherical polar coordinates thus reads,

$$
\left.
\begin{aligned}
\hat{L}_x &= \frac{\hbar}{i}\left(-\sin\varphi D_\theta - \cot\theta\cos\varphi D_\varphi\right) \\
\hat{L}_y &= \frac{\hbar}{i}\left(\cos\varphi D_\theta - \cot\theta\sin\varphi D_\varphi\right) \\
\hat{L}_z &= \frac{\hbar}{i} D_\varphi
\end{aligned}
\right\} \text{....[9]}
$$

Making use of the above results, the squares of the orbital angular momentum operators $\hat{L}_x^{\ 2}, \hat{L}_y^{\ 2}$ and $\hat{L}_z^{\ 2}$ can be obtained as:

$$\left.\begin{aligned}
\hat{L}_x^{\ 2} = -\hbar^2\Big[&\sin^2\varphi D_\theta^{\ 2} + \cot^2\theta\cos^2\varphi D_\varphi^{\ 2} \\
&+\cot\theta\cos^2\varphi D_\theta \\
&-\left(\sec^2\theta + \cot^2\theta\right)\sin\varphi\cos\varphi D_\varphi \\
&+2\cot\theta\sin\varphi\cos\varphi D_\theta D_\varphi\Big] \\
\hat{L}_y^{\ 2} = -\hbar^2\Big[&\cos^2\varphi D_\theta^{\ 2} + \cot^2\theta\sin^2\varphi D_\varphi^{\ 2} \\
&+\cot\theta\sin^2\varphi D_\theta \\
&+\left(\mathrm{cosec}^2\theta + \cot^2\theta\right)\sin\varphi\cos\varphi D_\varphi \\
&-2\cot\theta\sin\varphi\cos\varphi D_\theta D_\varphi\Big] \\
\hat{L}_z^{\ 2} = -\hbar^2 D_\varphi^{\ 2}&
\end{aligned}\right\} \quad [10]$$

then getting

$$\left.\begin{aligned}
\hat{L}^2 &= -\hbar^2\left[D_\theta^{\ 2} + \left(1+\cot^2\theta\right)D_\varphi^{\ 2} + \cot\theta D_\theta\right] \\
&= -\hbar^2\left[\left(D_\theta + \cot\theta\right)D_\theta + \mathrm{cosec}^2\theta D_\varphi^{\ 2}\right] \\
&= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \\
&= -\hbar^2\Omega
\end{aligned}\right\} \quad [11]$$

where Ω stands for

$$\Omega = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

To express the polar Laplacian operator

$$\nabla^2 = D_x{}^2 + D_y{}^2 + D_z{}^2 \qquad [12]$$

in spherical polar representation it is then necessary to obtain $D_x{}^2, D_y{}^2$ and $D_z{}^2$ ad functions of r, θ, φ. The Laplacian operator ∇^2 then reads,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\Omega}{r^2}$$

or

$$\nabla^2 = D_r{}^2 + \frac{2}{r}D_r - \frac{L^2}{\hbar^2 r^2} \qquad [13]$$

2. Separation of the Wave Equation

If the potential energy is spherically symmetric one, i.e. the potential is only a function of the magnitude of $\bar{r}$ measured from some origin, the wave equation can always be separated in spherical coordinates.

Having the wave equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V\left(\bar{r}\right)\right]\Psi\left(\bar{r}\right) = E\Psi\left(\bar{r}\right) \qquad [1]$$

with a spherically symmetric potential that can be

written in spherical coordinates as:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Psi(r)+V(\bar{r})\Psi(\bar{r})=E\Psi(\bar{r}) \quad \text{....[2]}$$

We first represent the radial and the angular parts by substituting

$$\Psi(\bar{r})=R(r)Y(\theta,\varphi) \quad \text{.....................................[3]}$$

into equation (2) and then dividing its two sides by $\Psi(\bar{r})$ to get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2mr^2}{\hbar^2}\right)[E-V(r)]=-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] \quad \text{.........[4]}$$

both sides must be equal to a constant that we call λ, since the left side of equation (4) depends only on r and the right side depends only on θ and φ. Therefore equation (4) gives us a radial equation as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2m}{\hbar^2}(E-V(r))-\frac{\lambda}{r^2}\right]R=0 \quad \text{.......[5]}$$

and an angular equation as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}+\lambda Y=0 \quad [6]$$

the equation (6) can be written in the form

$$\hat{L}^2 Y(\theta,\varphi)=\lambda\hbar^2 Y(\theta,\varphi) \quad [7]$$

where

$$\hat{L}^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

and we have used the notation $\lambda\hbar^2$ for the eigenvalue parameter of $\hat{L}^2$.

Equation (7) is the eigenvalue equation of the operator $\hat{L}^2$. Further, the equation (6) can be separated by substituting

$$Y(\theta,\varphi)=H(\theta)\Phi(\varphi) \quad [8]$$

into its then following the same procedure to obtain

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dH}{d\theta}\right)+\left(\lambda-\frac{m^2}{\sin^2\theta}\right)H=0 \quad [9]$$

$$\frac{d^2\Phi}{d\varphi^2}+m^2\Phi=0 \quad [10]$$

m^2 is a constant just as the constant λ in the equation (7)

3. Admissibility Conditions on Solutions

The constant λ and m^2 maybe any (real or complex) quantities. However, restrictions on them arise the admissibility conditions for wave functions that are imposed on $H(\theta)$ and Φ. Considering the latter firstly, one simply observes that equation (10) has $e^{-im\varphi}$ and $e^{im\varphi}$ as solution. Since values of φ differing by integer multiples of 2π therefore these solutions will satisfy the conditions of single-valued ness only if

$$e^{im\varphi} = e^{im(p+2\pi)} \quad i.e \quad e^{im\cdot 2\pi} = 1 \text{ ....} [11]$$

From the properties of the exponential functions, it is well known that equation (11) will be true if and only if m is a real integers as:

$$m = 0, \pm 1, \pm 2, \cdots \text{ ....} [12]$$

Thus the admissible solution of equation (10) are

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \text{ ....} [13]$$

Note that since both sings of m are included it as not necessary to mention $e^{-im\varphi}$ separately. The normalization constant $(2\pi)^{-1/2}$ is chosen in order that Φ be normalized to unity over the range of φ.

With this choice;

$$\int_0^{2\pi} \Phi_m^*(\varphi)\Phi_{m'}(\varphi)d\varphi = \delta_{mm'} \quad [14]$$

Note also that;

$$\hat{L}_z\Phi_m = -i\hbar\frac{\partial}{\partial\varphi}\Phi_m = m\hbar\Phi_m \quad [15]$$

$m\hbar$ is the eigenvalue of $\hat{L}_z$ and Φ_m is the corresponding eigenfunctions. In fact, not only Φ_m but also $Y(\theta,\varphi)$ is such an eigenfunction. Thus the eigenfunctions of $\hat{L}^2$ are also simultaneously eigenfunctions of $\hat{L}_z$.

Turing now to equation (9). It is convenient to substitute $\omega = \cos\theta$ and put

$$H(\theta) = P(\omega) \quad [16]$$

equation (9) then becomes

$$\frac{d}{d\omega}\left[\left(1-\omega^2\right)\frac{dP}{d\omega}\right] + \left(\lambda - \frac{m^2}{1-\omega^2}\right)P = 0 \quad [17]$$

since the domain of θ is $(0 \to \pi)$, the domain of ω is $(1 \to -1)$. Since equation (17) is a second order differential equation, it has two linearly independent solutions. Except for particular values of λ, both of these are infinite at $\omega = \pm 1$ and are not physically

acceptable. Putting

$$P(\omega)=\left(1-\omega^2\right)^{\frac{|m|}{2}}K(\omega) \qquad [18]$$

in equation (17) to get

$$\left(1-\omega^2\right)\frac{d^2K}{d\omega^2}-2\left(|m|+1\right)\omega\frac{dK}{d\omega} + \left[\lambda-|m|\left(|m|+1\right)\right]K=0 \qquad [19]$$

By assuming a series form of the solution of (19) as:

$$K(\omega)=\sum_{r=0}^{\infty}a_r\omega^r \qquad [20]$$

substituting this in equation (19) and equating to zero that coefficients of the various powers of ω to get:

$$(r+1)(r+2)a_{r+2}+\left[\left(\lambda-|m|\left(|m|+1\right)\right) -2r\left(|m|+1\right)-r(r-1)\right]a_r=0$$

$$\therefore a_{r+2}=\frac{\left(r+|m|\right)\left(r+|m|+1\right)-\lambda}{(r+1)(r+2)}a_r \qquad [21]$$

our series of K must contain only a finite number of terms in order that the series be convergent one. This can be done by placing

$$\lambda=\left(s'+|m|\right)\left(s'+|m|+1\right) \;; s'=0,1,2,\cdots$$

Introducing the new numbers

$$l=s'+|m| \quad ,l=|m|,|m|+1,|m|+2,\cdots$$

$$\lambda = l(l+1) \quad ,l = 0,1,2,\cdots \qquad [22]$$

where $\lambda = l(l+1)$ as $l = 0,1,2,\cdots$ one of the solution is finite at $\omega = \pm 1$, the other is not, such finite solution has the form

$$P(\omega) = \left[1-\omega^2\right]^{\frac{|m|}{2}} \sum_{r=0}^{l-|m|} a_r \omega^r \qquad [23]$$

where the coefficients are given by equation (21). The physically acceptable solutions as $m = 0$ are called the Legender polynomials $P_l(\omega)$. For m not necessarily being equaling zero, the physically acceptable solutions (23) with $\lambda = l(l+1)$ and $|m| \le l$, which are called associated Legender functions are expressible in terms of polynomials:

$$P_l^m(\omega) = \left(1-\omega^2\right)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\omega^{|m|}} P_l(\omega) \qquad [24]$$

The values $\lambda = l(l+1), l = 0,1,2,\cdots$ are the admissible values of the parameter λ, and the eigenvalues of $\hat{L}^2$ are therefore $\lambda\hbar^2 = l(l+1)\hbar^2$.

It may be observed that the values that m can take are limited by the values chosen for l as:

$$m = l, l-1, l-2, \cdots, -l+1, -l \qquad [25]$$

since, for a given l, m can take any of these $(2l+1)$

values, the eigenvalue of $\hat{L}^2$ is $(2l+1)$ - fold degenerate.

Now, we can rewrite equation (19) as

$$\left(1-\omega^2\right)\frac{d^2K}{d\omega^2}-2\left(|m|+1\right)\omega\frac{dK}{d\omega} + \left[l\,(l+1)-|m|\left(|m|+1\right)\right]K=0 \quad ......[26]$$

In fact, if $m=0$ the last equation reduces to the Legender equation, whose polynomial solution is the Legender polynomial $P_l(\omega)$.

Explicitly the Legender differential equation is given by:

$$\left(1-\omega^2\right)\frac{dP_l}{d\omega}-2\omega\frac{dP_l}{d\omega}+l\,(l+1)P_l=0 \quad ....[27]$$

which can be written in an alternative form as

$$\left[D_\omega\left(1-\omega^2\right)D_\omega+l\,(l+1)\right]P_l(\omega) \quad ....[28]$$

The associated Legender functions $P_l^m(\omega)$, which are defined by equation (24), satisfy the differential equation

$$\left[\left(1-\omega^2\right)D_\omega^2-2\omega D_\omega+l\,(l+1)-\frac{m^2}{1-\omega^2}\right]P_l^m(\omega)=0 \quad ......[29]$$

which may be expressed in alternative form

$$\left[D_\omega\left(1-\omega^2\right)D_\omega-2\omega D_\omega+l\,(l+1)-\frac{m^2}{1-\omega^2}\right]P_l^m(\omega)=0 \quad .[30]$$

The orthogonality of the associated Legender functions may be expressed as

$$\int_{-1}^{1} P_l^m(\omega) P_{l'}^m \, d\omega = \left(\frac{2}{2l+1}\right)\frac{(l+m)!}{(l-m)!}\delta_l^{l'} \quad \text{.............} [31]$$

The function $H(\theta)$ can be written as

$$H(\theta) = P(\omega) = const \, P_l^m(\cos\theta) \quad \text{.....................} [32]$$

Choosing the constant for normalization, we have for any l and m subject to the condition (22) and (25)

$$H_{lm}(\theta) = \left[\frac{(2l+1)(l-m)!}{2(l+m)!}\right]^{1/2} (-1)^m P_l^m(\cos\theta) \, . [33]$$

$$\int_{0}^{\pi} H_{lm}(\theta) H_{l'm}(\theta) \sin\theta \, d\theta = \delta_{ll'} \quad \text{........................} [34]$$

From the eigenfunction $\Phi(\varphi)$ and $H(\theta)$ we contract the eigenfunction $Y_{lm}(\theta,\varphi)$ of the eigenvalue problem (7) as

$$Y_{lm}(\theta,\varphi) = H_{lm}(\theta)\Phi_m(\varphi) \quad \text{..............................} [35]$$

$$Y_{lm}(\theta,\varphi) = N_{lm} e^{im\varphi} P_l^m(\cos\theta) \quad \text{..........................} [36]$$

The function $Y_{lm}(\theta,\varphi)$ are the well known *Spherical Harmonics*. The constant N_{lm} is the normalization constant.

4. Spherical Harmonics

We have seen that the spherical harmonics satisfy the eigenvalue problem of $\hat{L}^2$, and correspond to the eigenvalues $l(l+1)\hbar^2$.

Operating with $\hat{L}_z = \frac{\hbar}{i} D_\varphi$ on the spherical harmonics, to get

$$\hat{L}_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi) \quad \text{.............................} [37]$$

which is an eigenvalue problem for $\hat{L}_z$.

It then follows that $\Phi_m(\varphi)$ and thus $Y_{lm}(\theta,\varphi)$ is an eigenfunction of $\hat{L}_z$ with the eigenvalue $m\hbar$.

The spherical harmonic can then simultaneously be an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$ or any linear combination of these operators.

This result that the spherical harmonics being simultaneous eigenfunction for both $\hat{L}^2$ and $\hat{L}_z$ is due to the fact that $\hat{L}^2$ and $\hat{L}_z$ are commuting operators. We have seen that all the three components of $\hat{L}$ commute with $\hat{L}^2$:

$$\left[\hat{L}_x,\hat{L}^2\right] = \left[\hat{L}_y,\hat{L}^2\right] = \left[\hat{L}_z,\hat{L}^2\right] = 0$$

It is because of the commutativity of $\hat{L}^2$ and $\hat{L}_z$ that they possess a complete set of simultaneous

eigenfunctions. The eigenfunctions $Y_{lm}(\theta,\varphi)$ form an orthonormal set ·

$$\int Y^{*}_{lm}(\theta,\varphi)Y_{l'm'}(\theta,\varphi)d\Omega=\delta_{l}^{l'}\delta_{m}^{m'} \quad \text{.......................[38]}$$

$$\int_0^{2\pi}\int_0^{\pi} Y^{*}_{lm}(\theta,\varphi)Y_{l'm'}(\theta,\varphi)\sin\theta d\theta d\varphi=\delta_{l}^{l'}\delta_{m}^{m'} \quad \text{........[39]}$$

. The complete eigenfunction of $\hat{L}^2$.corresponding to the quantum numbers l and m, $Y_{lm}(\theta,\varphi)$ is given by:

$$Y_{lm}(\theta,\varphi)=\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2}(-1)^m P_l^m(\cos\theta)e^{im\varphi}$$

....[40]

The first few spherical harmonics are

$$Y_{00}=\left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_{10}=\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_{11}=-\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\varphi} \qquad Y_{1,-1}=\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\varphi}$$

$$Y_{20}=\left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta-1\right)$$

Thus the separation of the wave equation in spherical polar coordinates results in wave functions that are eigenfunctions of both the total angular momentum and the components of angular momentum along the polar axis.

The quantum number l is called the arbital –

angular momentum quantum number.

The quantum number m is called the magnetic quantum number.

5. Angular momentum In Stationary States of Systems with Spherical Symmetry

The knowledge of angular momentum eigenfunctions is of immediate utility in the study of the stationary states of spherically symmetric systems.

(a) A Particle in a Central potential; The Radial equation:

Consider now a particle moving in a central potential, i.e. a particle $V(r)$ which is a function of the radial coordinate only. Its Hamiltonian,

$$H = \frac{P^2}{2\mu} + V(r) \qquad [1]$$

commutes with $\hat{L}$ and hence with $\hat{L}^2$. Therefore, we can find a complete set of eigenfunctions of H which are simultaneously eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$ also we can take the energy eigenfunctions in the form

$$u(r,\theta,\varphi) = R(r) Y_{lm}(\theta,\varphi) \qquad [2]$$

A less direct way of arriving at the same result is

to write the eigenvalue equation $Hu = Eu$ explicitly as,

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right]u = Eu \text{ ....} [3]$$

and rewrite it as,

$$-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2}\right]u + V(r)u = Eu \text{ ....} [4]$$

and then separate it into radial and angular parts by substituting $u = R(r)Y(\theta,\varphi)$.

The separation is done exactly as before. Since

$$\hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)\hbar^2 Y_{lm}(\theta,\varphi) \text{ ....} [5]$$

we obtain, the following ordinary differential equation for $R(r)$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0 . [6]$$

The eigenvalue problem for a spherically symmetric potential thus reduces to determining for what values of E the radial wave equation has admissible solutions, and then finding the solutions.

(b) The Radial Wave Function

It is often to write

$$R(r) = \frac{1}{r}\mathrm{X}(r) \text{ ....} [7]$$

because it enables the radial wave equation to be reduced to a simpler form

$$\frac{d^2\mathrm{X}}{dr^2}+\left[\frac{2\mu}{\hbar^2}(E-V)-\frac{l(l+1)}{r^2}\right]\mathrm{X}=0 \quad \text{..............} [8]$$

The behavior of the wave function near the origin can readily be shown from this equation.
For any $l \neq 0$, the centrifugal term diverges rapidly as $r \to 0$ and dominates over the other terms.
Thus in the neighborhood of the origin and as good approximation admits $\mathrm{X}=const.r^{(l+1)}$ and $\mathrm{X}=const.r^{-l}$ as solutions. The latter is not acceptable since it makes $R(r)$ to diverge as $r \to 0$. The other solution leads to

$$R(r)=cons.r^l \quad as\ r \to 0 \quad \text{............................} [9]$$

Thus any acceptable solution, for angular momentum l, must behave like r^l near the origin. It is necessary to knows also the asymptotic behavior of radial wave functions.
As $r \to \infty$ the radial equation reduces to

$$\frac{d^2\mathrm{X}}{dr^2}+\frac{2\mu E}{\hbar^2}\mathrm{X}\approx 0 \quad ,(r\to\infty) \quad \text{..........................} [10]$$

this is satisfied by $\mathrm{X}=e^{-\alpha r}$ where $\alpha^2=-2\mu E/\hbar^2$. Thus the dominatest asymptotic behavior of R is like

$$R(r) \approx cons.r^n e^{-\alpha r} \qquad ,(r \to \infty), \alpha^2 = \frac{-2\mu E}{\hbar^2} \text{....} [11]$$

where n is positive.

We observe that in the special case of s-state $(l = 0)$ the radial equation is identical as the form of the Schrödinger equation in one dimension. The norm of the wave function u, when being expressed in spherical polar coordinates, is evidently given by:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |u(r,\theta,\varphi)|^2 d\varphi \cdot \sin\theta d\theta \cdot r^2 dr \text{ .... } [12]$$

when u is factorized into $R(r)Y(\theta,\varphi)$ the norm reduces to

$$\int_0^\infty |R(r)|^2 r^2 dr \text{ .... } [13]$$

The Two Particle Problem

Consider a system of two interacting particles, the atomic nucleus of charge ze and the electron of charge $-e$. But if the nucleus is supposed to remain static, the Schrödinger equation is just that for a single particle, the electron is then moving in a potential $V(r) = \frac{-ze^2}{r}$.

Actually when the atom as a whole in at rest, it is not the nucleus, but the center of mass of the two-

particle system which remains static. However, this fact can be taken into account by using, in the kinetic energy term in the Hamiltonian, the reduced mass μ instead of the electron mass.

The classical Hamiltonian function for two particle system with central force interaction is

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V\left(\overline{r}_1 - \overline{r}_2\right) \text{.........................} [1]$$

where $m_1 r_1, P_1$ and m_2, r_2, P_2 refer to the masses, the position vectors and momenta of the two particles 1 and 2, while $V\left(\underline{r}_1, \underline{r}_2\right)$ is their mutual interaction, which is a function of their distance $|\underline{r}_1 - \underline{r}_2|$ only.
The procedure is to replace the momenta $\overline{P}_i$ by its quantum mechanical angular $\frac{\hbar}{i}\underline{\nabla}_i$, and consequently we get:

$$\hat{H} = -\frac{\hbar}{2m_1}\nabla_{r_1}^2 - \frac{\hbar}{2m_2}\nabla_{r_2}^2 + V\left(|\underline{r}_1 - \underline{r}_2|\right) \text{............} [2]$$

If we assume that the two particle system is described by a wave function $\Psi\left(\overline{r}_1, \overline{r}_2, t\right)$, then we have:

$$\left.\begin{array}{l} \left(\hat{H} - E\right)\Psi\left(\overline{r}_1, \overline{r}_2, t\right) = 0 \\ \left(\hat{H} - i\hbar D_t\right)\Psi\left(\overline{r}_1, \overline{r}_2, t\right) = 0 \end{array}\right. \text{..............................} [3]$$

If we spell out the explicit expression $\hat{H}$ which is given by equation (2) the above equation becomes:

$$\left[-\frac{\hbar^2}{2m_1}\nabla^2_{r_1}-\frac{\hbar^2}{2m_2}\nabla^2_{r_2}+V\left(|\underline{r}_1-\underline{r}_2|\right)-i\hbar D_t\right]\Psi\left(\overline{r_1},\overline{r_2},t\right)=0 \quad \text{.......} [4]$$

where

$$\nabla^2_{r_i}=\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2} \quad ,i=1,2$$

The equation (4) which describes the two equivalent one particle problems, in which the motion of the center of mass and the relative motion are treated separately. This separation is accomplished by changing the variables $\overline{r_1},\overline{r_2}$ to $\overline{R},\overline{r}$, such that

$$\overline{R}=\frac{m_1\overline{r_1}+m_2\overline{r_2}}{m_1+m_2} \quad ,R=(X,Y,Z) \text{ ....} [5]$$

is the position vector of the center of mass, and

$$\overline{r}=\overline{r_1}-\overline{r_2} \quad ,\overline{r}=(x,y,z)\text{.......} [6]$$

is the separation between the two particles.

We shall now prove that

$$-\frac{\hbar^2}{2m_1}\nabla^2_{r_1}-\frac{\hbar^2}{2m_2}\nabla^2_{r_2}=-\frac{\hbar^2}{2M}\nabla^2_R-\frac{\hbar^2}{2\mu}\nabla^2_r \text{.......} [7]$$

where $M=m_1+m_2$, $\mu=\frac{m_1m_2}{m_1+m_2}$, μ is called the

reduced mass.

If $\Psi(R,r)=\Psi(X,Y,Z,x,y,z)$

$$\frac{\partial\Psi}{\partial x_1}=\frac{\partial\Psi}{\partial X}\frac{\partial X}{\partial x_1}+\frac{\partial\Psi}{\partial x}\frac{\partial x}{\partial x_1}$$

$$=\frac{m_1}{m_1+m_2}\frac{\partial\Psi}{\partial X}+\frac{\partial\Psi}{\partial x}$$

$$\frac{\partial\Psi}{\partial x_2}=\frac{m_2}{m_1+m_2}\frac{\partial\Psi}{\partial X}-\frac{\partial\Psi}{\partial x}$$

$$\left.\begin{aligned}\therefore\frac{\partial}{\partial x_1}&=\frac{\mu}{m_2}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}\\ \frac{\partial}{\partial x_2}&=\frac{\mu}{m_1}\frac{\partial}{\partial X}-\frac{\partial}{\partial x}\end{aligned}\right\}\quad\text{.................................. [8]}$$

Then

$$\left.\begin{aligned}\therefore\nabla_{r_1}&=\frac{\mu}{m_2}\nabla_R+\nabla_r\\ \nabla_{r_2}&=\frac{\mu}{m_1}\nabla_R-\nabla_r\end{aligned}\right\}\quad\text{.................................. [9]}$$

where the operator ∇_R operates on the coordinates (X,Y,Z) of the center of mass, ∇_r operates on the coordinates (x,y,z) of the electron relative to the nucleus.

Equation (7) gives

$$-\frac{\hbar^2}{2m_1}\left(\frac{\mu}{m_2}\nabla_R+\nabla_r\right)^2-\frac{\hbar^2}{2m_2}\left(\frac{\mu}{m_1}\nabla_R-\nabla_r\right)^2$$
$$=-\frac{\hbar^2\mu^2}{2m_1m_2^{\,2}}\nabla_R^2-\frac{\hbar^2\mu^2}{2m_2m_1^{\,2}}\nabla_R^2-\frac{\hbar^2}{2m_1}\nabla_r^2-\frac{\hbar^2}{2m_2}\nabla_r^2$$
$$=-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2$$

Then, the equation (4) can be written in the form:

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2+V\left(|r|\right)\right]\Psi(R,r)=E\Psi(R,r) \quad [10]$$

the last equation shows that the wave function $\Psi(R,r)$ can be written in the form

$$\Psi(R,r)=\Phi(\underline{R})u(\underline{r}) \quad \ldots\ldots [11]$$

From the two equations (10), (11) we can write Schrödinger equation in the form:

$$-\frac{\hbar^2}{2M}u(r)\nabla_R^2\Phi(R)-\frac{\hbar^2}{2\mu}\Phi(R)\nabla_r^2u(r)$$
$$+V\left(|r|\right)\Phi(R)u(r)=E\Phi(R)u(r)$$

the energy E represent the total energy of the system (the atom). By the usual procedure, one finds that $\Phi(R)$ and $u(r)$ satisfy the equations:

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2-E_R\right]\Phi(\underline{R})=0 \quad \ldots\ldots [12]$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V\left(|r|\right) - E_r\right]u\left(\bar{r}\right) = 0 \text{ ....} [13]$$

where

$$E_R + E_r = E \text{ ....} [14]$$

and E_R is the energy associated to the free motion of the centre of mass, and E_r is the kinetic energy of the electron relative to the nucleus.

The R -equation (12) is exactly the same as Schrödinger wave equation for a free particle of mass M , which representable motion of centre of mass, while the r -equation (13) describes the relative motion as an equivalent particle of reduced mass μ moving in a fixed central field $V\left(|r|\right)$.

The Radial wave Equation:

We now proceed to solve the three dimension Schrödinger wave equation:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\bar{r}}^2 + V\left(|\bar{r}|\right) - E_r\right]u\left(\bar{r}\right) = 0 \text{ ....} [15]$$

for spherically symmetric potential. It is natural to employ for spherically symmetric potential, it is natural to employ the spherical polar coordinates (r,θ,φ)

$$\nabla_{\bar{r}}^2 = D_r^2 + \frac{2}{r}D_r - \frac{\hat{L}^2}{\hbar^2 r^2} \text{ ....} [16]$$

and consequently the above wave equation becomes:

$$-\frac{\hbar^2}{2\mu}\left[\left(D_r^2+\frac{2}{r}D_r-\frac{\hat{L}^2}{\hbar^2 r^2}\right)+V(r)-E_r\right]u(\bar{r})=0$$

By the usual procedure, by substituting

$$u(\bar{r})=R(r)Y(\theta,\varphi) \quad \text{[17]}$$

in the last equation and then dividing both sides on $u(\bar{r})$, we can get:

$$\left[-\frac{\hbar^2}{2\mu}\left(D_r^2+\frac{2}{r}D_r-\frac{l(l+1)}{r^2}\right) -\frac{l(l+1)}{r^2}+V(r)-E_n\right]R_{nl}(r)=0 \quad \text{[18]}$$

equation (18) specifies the so-called "radial equation", where

$$\hat{L}^2 Y(\theta,\varphi)=l(l+1)\hbar^2 Y(\theta,\varphi) \quad \text{[19]}$$

Now to get rid of the term $\frac{2}{r}D_r$ we introduce the transformation

$$\Phi_{nl}(r)=rR_{nl}(r) \quad \text{[20]}$$

for which the radial equation (18) becomes:

$$\left[-\frac{\hbar^2}{2\mu}D_r^2+\left(V(r)+\frac{l(l+1)}{2\mu r^2}\right)-E_n\right]\Phi_{nl}(r)=0 \quad \text{[21]}$$

This is the Schrödinger wave equation for one

dimensional motion under the influence of an effective potential

$$V_{eff}(r)=V(r)+\frac{l(l+1)}{2\mu r^2} \quad \text{[22]}$$

The second term of the R.H.S. of the above equation is called the centrifugal potential.

It is to be noted that the radial equation (21) has significance only for positive values of r and by replacing to equation (20) we see that the boundary condition to be specified by the function $\Phi_{nl}(r)$ at the origin $r=0$ is that

$$\Phi_{nl}(r)=0 \quad \text{[23]}$$

otherwise the radial function R_{nl} would be divergent at the origin. The radial wave function satisfies the equation which can be written in the form:

$$\left[-\frac{\hbar^2}{2\mu}\left(D_r^2-\frac{l(l+1)}{r^2}\right)+V(r)+|E_{nl}|\right]\Phi_{nl}(r)=0 \quad \text{[24]}$$

The Attractive Coulomb Potential

The attractive coulomb interaction between a positive charge z_1e and a negative charge $-z_2e$ is given by:

$$V(r)=-\frac{z_1z_2e^2}{r} \quad \text{[1]}$$

This potential provides another bound state problem which can be solved analytically.

The corresponding radial wave equation is thus:

$$\left[-\frac{\hbar^2}{2\mu}\left(D_r^2-\frac{l(l+1)}{r^2}\right)-\frac{z_1z_2e^2}{r}+|E_{nl}|\right]\Phi_{nl}(r)=0$$

.... [2]

If we use the transformation $\rho=q\,r$, the above equation becomes:

$$\left[D_\rho^2-\frac{l(l+1)}{\rho^2}-\frac{2\mu z_1z_2e^2}{\hbar^2 q\,\rho}-\frac{2\mu|E_{nl}|}{\hbar^2q^2}\right]\Phi_{nl}(\rho)=0 \quad [3]$$

and if we take,

$$q^2=\frac{8\mu}{\hbar^2}|E_{nl}| \quad \text{.......................................} [4]$$

$$\alpha=\frac{2\mu z_1z_2e^2}{\hbar^2 q} \quad \text{.......................................} [5]$$

we find that

$$\left[D_\rho^2-\frac{l(l+1)}{\rho^2}+\frac{\alpha}{\rho}-\frac{1}{4}\right]\Phi_{nl}(\rho)=0 \quad \text{..................} [6]$$

Let us now transform the function $\Phi_{nl}(\rho)$, such that,

$$\Phi_{nl}(\rho)=\Omega\varphi_{nl}(\rho) \quad \text{.......................................} [7]$$

$$\begin{aligned}D_\rho^2\Phi_{nl}(\rho)&=D_\rho^2\left(\Omega\varphi_{nl}(\rho)\right)\\&=D_\rho\left[\Omega\varphi'+\varphi\Omega'\right]\\&=\Omega\varphi''+2\varphi'\Omega'+\varphi\Omega''\end{aligned}$$

$$\therefore D_\rho^2\Phi_{nl}(\rho)=\left[\Omega D_\rho^2+2\Omega' D_\rho+\Omega''\right]\varphi(\rho)\text{........}[8]$$

$$\therefore\left[D_\rho^2+2\frac{\Omega'}{\Omega}D_\rho+\frac{\Omega''}{\Omega}-\frac{l(l+1)}{\rho^2}+\frac{\alpha}{\rho}-\frac{1}{4}\right]\varphi(\rho)=0$$

$$\text{..}[9]$$

If we take Ω in the form

$$\Omega=e^{\beta\rho}\rho^\gamma\text{..}[10]$$

we get,

$$\frac{\Omega'}{\Omega}=\beta+\frac{\gamma}{\rho}\ ,\frac{\Omega''}{\Omega}=\left(\beta+\frac{\gamma}{\rho}\right)^2-\frac{\gamma}{\rho^2}=\beta^2+\frac{2\beta\gamma}{\rho}+\frac{\gamma(\gamma-1)}{\rho^2}$$

and the above equation becomes:

$$\left[D_\rho^2+2\left(\beta+\frac{\gamma}{\rho}\right)D_\rho+\frac{\gamma(\gamma-1)-l(l+1)}{\rho^2}+\frac{\alpha+2\beta\gamma}{\rho}+\beta^2-\frac{1}{4}\right]\varphi(\rho)=0\text{....}[11]$$

To get rid of terms in ρ^{-2} and β we chose β,γ such that

$$\gamma(\gamma-1)-l(l+1)=0\text{..}[12]$$

$$\beta^2-\frac{1}{4}=0\text{..}[13]$$

$$\Rightarrow\beta=\begin{cases}-1/2\\+1/2\end{cases}\qquad,\gamma=\begin{cases}l+1\\-l\end{cases}$$

If we consider the values $\beta=-1/2\ ,\gamma=(l+1)$, we get final for the differential equation (11)

$$\left[D_\rho^2+2\left(\frac{l+1}{\rho}-\frac{1}{2}\right)D_\rho+\frac{\alpha-l-1}{\rho}\right]\varphi_{nl}(\rho)=0 \quad [14]$$

At this point let us introduce the associated Lagurre equation which has the form:

$$\left[D_z^2+\left(\frac{p+1}{z}-1\right)D_z-\frac{(p-q)}{z}\right]L_q^p(z)=0 \quad [15]$$

whose solution $L_q^p(z)$ is so-called associated Lagurre polynomial.

Comparing (14), (15)

$$\therefore \varphi_{nl}(\rho)=L_n^{2l+1}(\rho) \quad [16]$$

in which n is an integer and is given by:

$$n=\alpha+l \quad [17]$$

Consequently the original eigenfunctions $\Phi_{nl}(\rho)$ is given by:

$$\Phi_{nl}(\rho)=\Omega\varphi_{nl}(\rho)=e^{-\frac{\rho}{2}}\rho^{l+1}L_n^{2l+1}(\rho) \quad [18]$$

$$\alpha=(n-l)=\frac{2\mu z_1 z_2 e^2}{\hbar^2 q}$$

$$q=\frac{2\mu z_1 z_2 e^2}{\hbar^2(n-l)}$$

$$|E_{nl}|=\frac{\hbar^2}{8\mu}q^2=\frac{\hbar^2}{8\mu}\cdot\frac{4\mu^2 z_1^2 z_2^2 e^4}{\hbar^2(n-l)^2}$$

$$\therefore |E_{nl}| = -\frac{\mu z_1^2 z_2^2 e^4}{2\hbar^2 (n-l)^2} \quad \text{.....................................} [19]$$

When $z_1 = z_2 = 1$

$$\therefore E_{nl} = -\frac{\mu e^4}{2\hbar^2 (n-l)^2} \quad \text{.....................................} [20]$$

The equations (18), (20) are the solution of the considered problem and gives the eigenfunctions and the corresponding eigenvalues.

Examples

Example (1)

A particle in one-dimensional potential well $0 \le x \le a$ for which

$$V = \begin{cases} \infty & x \le 0 \\ 0 & 0 \le x \le a \\ \infty & x \ge a \end{cases}$$

Solve the time – independent Schrödinger equation for this case.

Solution

$V = 0$	$V = 0$	$V = \infty$
Ψ_1	Ψ_2	Ψ_3
	$x = 0$	$x = a$

For the region $x \le 0$

$$\frac{d^2\Psi_1}{dx^2} + \frac{2m}{\hbar^2}(E - V) = 0$$

Since $V \to \infty$

Then the curvature of the rate of change of slope becomes extremely great, thus at $x \ge a$

Then we must put:

$\Psi_3 = 0 \quad at \quad x = a$

$\Psi_1 = 0 \quad at \quad x = 0$

In the region $0 \le x \le a$ we put $V = 0$, we have:

$$\frac{d^2\Psi_2}{dx^2}+\frac{2m}{\hbar^2}(E)\Psi_2=0$$

Let $\frac{2m}{\hbar}E=k^2$, then

$$\left(D^2+k^2\right)\Psi_2=0$$

$$\lambda^2=-k^2$$

$$\therefore \lambda=\pm ik$$

$$\therefore \Psi_2=Ae^{ikx}+Be^{-ikx}$$

$$=A(\cos kx+i\sin kx)+B(\cos kx-i\sin kx)$$

$$=(A+B)\cos kx+(A-B)i\sin kx$$

$$\Psi_2=A'\cos kx+B'\sin kx$$

where $A'=A+B \quad ,B'=i(A-B)$

Since the wave function must be continuous in space for this we put:

$$\Psi_1(0)=\Psi_2(0) \text{ at } x=0$$

$$\therefore 0=A'\cos k(0) \quad \Rightarrow A'=0$$

$$\therefore \Psi_2=B'\sin kx$$

Also since the wave function must be continuous at $x=a$

$$\Psi_2(a)=\Psi_3(a)$$

$$\therefore B'\sin kx=0 \quad \Rightarrow B'\neq 0$$

$$\therefore \sin ka=0$$

$$ka=n\pi \quad ,n=1,2,3,\cdots$$

Since $k^2 = \frac{2m}{\hbar^2}E \quad , k = \frac{n\pi}{a}$

$$\therefore \frac{n^2\pi^2}{a^2} = \frac{2m}{\hbar^2}E \qquad \therefore E_n = \frac{n^2\pi^2\hbar^2}{2a^2m}$$

$$\Psi_2 = B'\sin\left(\frac{n\pi}{a}x\right)$$

The normalization condition;

$$\int_{-\infty}^{\infty} \Psi\Psi^* dx = 1$$

$$|B^2|\int_0^a \sin^2\frac{n\pi}{a}x\,dx = 1$$

$$\frac{1}{2}|B^2|\int_0^a\left(1-\cos\frac{2n\pi}{a}x\right)dx = 1$$

$$\frac{1}{2}|B^2|\left[x - \frac{a}{2n\pi}\sin\frac{2n\pi}{a}x\right]_0^a = 1$$

$$\therefore \frac{1}{2}|B^2|a = 1 \quad \Rightarrow B = \sqrt{2/a}$$

Then the wave function is specified at any point in the space

$$\Psi_1 = 0 \quad , \Psi_2 = \sqrt{2/a}\sin\frac{n\pi}{a}x \quad , \Psi_3 = 0$$

Example (2)

Find the mean value of x an P_x for the particle in the previous problem.

Solution

$$\langle x\rangle = \int_0^a \Psi^* x \Psi \, dx \quad = \frac{a}{2}$$

$$= \int_0^a x\Psi^2 dx = \frac{2}{a}\int_0^a x \sin^2 \frac{n\pi}{a} x \, dx$$

$$= \frac{2}{a}\int_0^a \frac{1}{2} x \left(1 - \cos\frac{2n\pi}{a} x\right) dx$$

$$= \frac{1}{a}\left[\frac{a^2}{2} - \int_0^a x \cos\frac{2n\pi}{a} x \, dx\right]$$

$$= \frac{1}{a}\left[\frac{a^2}{2} - \left\{\frac{ax}{2n\pi}\sin\frac{2n\pi}{a}x\right\}_0^a + \frac{a}{2n\pi}\int_0^a \sin\frac{2n\pi}{a} x \, dx\right]$$

$$= \frac{1}{a}\left[\frac{a^2}{2} - zero - \frac{a^2}{(2n\pi)^2}\left(\cos\frac{2n\pi}{a}\right)_0^a\right]$$

$$\therefore \langle x\rangle = \frac{a}{2}$$

The expectation value of P_x is:

$$\langle P_x\rangle = \int_0^a \Psi^* \left(1 - i\hbar\frac{\partial}{\partial x}\right)\Psi \, dx$$

$$= -\frac{2i\hbar n\pi}{a^2}\cdot\frac{1}{2}\int_0^a \sin\frac{2n\pi}{a} x \, dx$$

$$= \frac{i\hbar n\pi}{a^2}\cdot\frac{a}{2n\pi}\left(\cos\frac{2n\pi}{a} x\right)_0^a$$

$$= zero$$

Example (3)

Find the energy levels and the wave functions of a particle in a one-dimensional coulomb potential well

$$V(x) = -\frac{e^2}{|x|}$$

Solution

Schrödinger wave equation has the form;

$$-\frac{\hbar}{2m}\frac{d^2\Psi}{dx^2} - \frac{e^2}{|x|}\Psi = E\Psi \quad \text{..................................} [1]$$

For $E > 0$ will have a continuous spectrum.

Let us consider the case of $E < 0$.

We denote $\gamma^2 = -\frac{2mE}{\hbar^2}$ $,\chi\frac{me^2}{\hbar^2\gamma}$ and introduce the new variable $\xi = 2\gamma x$

Now we can write the equation in dimensionless variables $\xi = 2\gamma x$

$$\frac{d\Psi}{dx} = \frac{d\Psi}{d\xi}\frac{d\xi}{dx} = 2\gamma\frac{d\Psi}{d\xi},$$

$$\frac{d^2\Psi}{dx^2} = \frac{d}{d\xi}\left(\frac{d\Psi}{dx}\right)\frac{d\xi}{dx} = 4\gamma^2\frac{d^2\Psi}{d\xi^2}$$

Substituting into equation (1) we have

$$\frac{d^2\Psi}{d\xi^2}-\left(\frac{\gamma e^2}{2E|\xi|}+\frac{1}{4}\right)\Psi=0 \quad [2]$$

But

$$-\frac{\gamma e^2}{2E}=-\frac{\gamma^2\hbar^2\chi}{2mE}=\frac{2mE}{\hbar^2}\cdot\frac{\hbar^2\chi}{2mE}=\chi \quad [3]$$

From equations (2) and (3) we obtain

$$\frac{d^2\Psi}{d\xi^2}+\left(\frac{\chi}{|\xi|}-\frac{1}{4}\right)\Psi=0 \quad [4]$$

First let us consider that in the region $\xi>0$ we have

$$\frac{d^2\Psi}{d\xi^2}+\left(\frac{\chi}{\xi}-\frac{1}{4}\right)\Psi=0 \quad [5]$$

When $\xi\to\infty$, the equation becomes

$$\frac{d^2\Psi_\infty}{d\xi^2}-\frac{1}{4}\Psi_\infty=0 \quad [6]$$

Equation (6) has the solution

$$\Psi_\infty=Ae^{-\frac{1}{2}\xi}+Be^{\frac{1}{2}\xi} \quad [6^*]$$

But since $\xi\to\infty$, we must put $B=0$ in equation (6*), we have

$$\Psi_\infty=Ae^{-\frac{1}{2}\xi} \quad [7]$$

We introduce the function $f(\xi)$ and substitute

$$\Psi=e^{-\frac{1}{2}\xi}f(\xi)$$

into equation (5) we give

$$\xi\frac{d^2f}{d\xi^2}-\xi\frac{df}{d\xi}+\chi f=0 \quad\text{.......}\quad [8]$$

To study the behavior fo $f(\xi)$ near $\xi=0$ we substitute $f(\xi)=\xi^{\alpha}$ in the equation (8) we find that

$$\alpha(\alpha-1)\xi^{\alpha-1}-\alpha\xi^{\alpha}+\chi\xi^{\alpha}=0$$

Equating coefficients of $\xi^{\alpha-1}$

$$\therefore \alpha(\alpha-1)=0$$

$$\alpha=0 \quad or \quad \alpha=1$$

There are two solutions

(i) $f(\xi)=1$ .... [9]

(ii) $f(\xi)=\xi$ .... [10]

The first solution can be used however, since at $\xi=0$, equation (8) gives

$\chi f(\xi)=0$ .... [11]

For this reason we take

$$f(\xi)=\xi$$

If we put $f(\xi)=\sum_{k=1}^{\infty}a_k\xi^k$ in the equation (8)

$$\sum_{k=1}^{\infty}\left\{a_k k(k-1)\xi^{k-1}-a_k k\xi^k+\chi a_k\xi^k\right\}=0$$

Equating the coefficients of ξ^k we have

$$a_{k+1}(k+1)k - a_k(k-\chi) = 0$$

$$\therefore a_{k+1} = a_k \frac{k-\chi}{k(k-1)} \quad ,k = 1,2,3,\cdots$$

Next we take the limit of this formula for $k \gg 1$ then

$$(a_{k+1})_{k\gg1} = \left(a_k \frac{k-\chi}{k(k+1)}\right)_{k\gg1}$$

$$= a_k \lim_{k\to\infty} \frac{k-\chi}{k(k+1)}$$

$$= a_k \lim_{k\to\infty} \frac{1}{1+2k} = 0$$

Then for $k = n \Rightarrow a_{n+1} = 0$

$$k - \chi = 0 \quad ,k = \chi = n$$

i.e. $$n = \chi = \frac{me^2}{\hbar^2\gamma} \cdot \frac{\hbar}{\sqrt{-2mE}}$$

We get discrete energy spectrum, since

$$n^2 = \frac{-m^2e^4}{\hbar^4} \cdot \frac{\hbar^2}{2mE} = -\frac{me^4}{2\hbar^2 E}$$

$$\therefore E_n = \frac{-me^4}{2\hbar^2 n^2}$$

For $\Psi = e^{-\frac{1}{2}\xi} f(\xi)$ to be finite, $f(\xi)$ must become a polynomial, and this is possible when its series expansion is cut off at the n^{th} number

$$f(\xi)=\sum_{k=1}^{n}a_k\xi^k.$$

$$=a_1\xi+a_2\xi^2+a_3\xi^3+...+a_n\xi^n$$

$$=\xi\left[a_1+a_2\xi+a_3\xi^2+...+a_n\xi^{n-1}\right]=\xi\sum_{l=0}^{n-1}a_{l+1}\xi^l$$

$$\Psi=e^{-\frac{1}{2}\xi}f(\xi)=e^{-\frac{1}{2}\xi}\xi\sum_{l=0}^{n-1}a_{l+1}\xi^l$$

Example (4)

Solve Schrödinger wave equation for a three dimensional spherically symmetric harmonic oscillator with potential energy $V(r)=\frac{1}{2}\mu\omega^2r^2$

Solution

To find the wave function Ψ for the spherically symmetric oscillator, Let Ψ in the form

$$\Psi(r,\theta,\varphi)=f(r)Y(\theta,\varphi)\quad\text{..................................... [1]}$$

Schrödinger wave equation has the form,

$$\nabla^2\Psi+\frac{2\mu}{\hbar^2}(E-V(r))\Psi=0$$

$$\nabla^2\Psi+k^2(r)\Psi=0\quad\text{..................................... [2]}$$

Where $k^2(r)=\sqrt{\frac{2\mu}{\hbar^2}\left[E-V(r)\right]}$

But $\nabla^2\Psi$ in the spherical polar coordinates has the form

$$\nabla^2\Psi = \nabla_r^{\ 2}\Psi + \frac{1}{r^2}\nabla_{\theta,\varphi}^{\ 2}\Psi \quad \text{.................................. [3]}$$

Where

$$\nabla_r^{\ 2} = \frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \quad \text{.. [4]}$$

$$\nabla_{\theta,\varphi}^{\ 2} = \frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta} + \frac{1}{\sin^2\theta}\frac{d^2}{d\varphi^2} \quad \text{................. [5]}$$

From equations (1), (2), (3), (4) and (5) we have

$$\nabla_r^{\ 2} f(r) + \left[k^2(r) - \frac{\lambda}{r^2}\right] f(r) = 0 \quad \text{........................ [6]}$$

$$\nabla_\theta^{\ 2} f(\theta) + \left[\lambda - \frac{m^2}{\sin^2\theta}\right] f(\theta) = 0 \quad \text{........................ [7]}$$

$$\nabla_\varphi^{\ 2} f(\varphi) + m^2 f(\varphi) = 0 \quad \text{.................................... [8]}$$

Where $\nabla_\theta^{\ 2} = \frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}$

$$\nabla_\varphi^{\ 2} = \frac{d^2}{d\varphi^2}$$

By using equation (7) we obtain that

$$\lambda = l(l+1) \quad \text{.. [9]}$$

Substituting in equation (6) we have

$$\nabla_r^{\ 2} f(r) + \left[k^2(r) - \frac{l(l+1)}{r^2}\right] f(r) = 0 \quad \text{................ [10]}$$

The radial equation (10) have the form;

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2f}{dr^2}\frac{2}{r}\frac{df}{dr}-\frac{l(l+1)}{r^2}f\right]+\frac{1}{2}\mu\omega^2r^2f(r)=Ef(r)$$

.... [11]

Where $V=\frac{1}{2}\mu\omega^2r^2$

We introduce the new function

$$U=rf(r) \quad ,\therefore f(r)=\frac{U}{r}$$

$$\frac{df}{dr}=\frac{rU'-U}{r^2}=\frac{U'}{r}-\frac{U}{r^2}$$

$$\frac{d^2f}{dr^2}=\frac{1}{r^4}\left[r^2(rU''+U'-U')-2r(rU'-U)\right]$$

$$=\frac{U''}{r}-\frac{2U'}{r^2}+\frac{2U}{r^3}$$

Substituting in equation (11) we obtain;

$$U''-\frac{l(l+1)}{r^2}U-\frac{\mu^2\omega^2}{\hbar^2}r^2U+\frac{2\mu E}{\hbar^2}U=0 \text{ .... [11a]}$$

Where

$$U''=\frac{d^2U}{dr^2}$$

We introduce a new parameter ξ such that

$$\xi=r\sqrt{\frac{\mu\omega}{\hbar}}=ra \quad ,a=\sqrt{\frac{\mu\omega}{\hbar}}$$

Therefore

$$U' = \frac{dU}{dr} = \frac{dU}{d\xi}\frac{d\xi}{dr} = a\frac{dU}{d\xi}$$

$$U'' = \frac{d^2U}{dr^2} = a^2\frac{d^2U}{d\xi^2}$$

Substituting in equation (11-a) we get

$$a^2\frac{d^2U}{d\xi^2} - \frac{l(l+1)}{\xi^2}a^2U - r^2a^4U + \frac{2\mu E}{\hbar^2}U = 0 \text{ .... [11b]}$$

Where $a^4 = \mu^2\omega^2/\hbar^2$.

$$\therefore \frac{d^2U}{d\xi^2} - \frac{l(l+1)}{\xi^2}U - r^2a^2U + \frac{2\mu E\hbar}{\hbar^2\mu\omega}U = 0$$

$$\frac{d^2U}{d\xi^2} - \frac{l(l+1)}{\xi^2}U - \xi^2U + \frac{2E}{\hbar\omega}U = 0$$

By putting $\lambda = E/\hbar\omega$

$$\therefore \frac{d^2U}{d\xi^2} - \frac{l(l+1)}{\xi^2}U - \xi^2U + 2\lambda U = 0 \text{ .... [11c]}$$

Therefore

$$\frac{d^2U}{d\xi^2} + \left[2\lambda - \frac{l(l+1)}{\xi^2} - \xi^2\right]U = 0 \text{ .... [12]}$$

as $\xi \to \infty$

we see that $\xi^2 \gg 2\lambda$.

Therefore the equation (12) takes the form

$$\frac{d^2U_\infty}{d\xi^2} - \xi^2U_\infty = 0$$

Which has the solution

$U_{\infty} = e^{-\frac{1}{2}\xi^2}$ .... [13]

And when $\xi \to 0$ we seek the solution $U_0 = \xi^{\alpha}$ and substituting in equation (12) we have

$$\alpha(\alpha-1)\xi^{\alpha-2} + \left[2\lambda - \frac{l(l+1)}{\xi^2} - \xi^2\right]\xi^{\alpha} = 0$$

Equating the coefficients of $\xi^{\alpha-2}$ by zero we have

$$\alpha(\alpha-1) = l(l+1)$$

Which gives $\alpha = -l$, $\alpha = l+1$

Therefore the solution of the equation (12) when $\xi \to 0$ gives as

$U_0 = \xi^{l+1}$ .... [14]

Then the complete solution of the equation (12) can be written as

$U(\xi) e^{-\frac{1}{2}\xi^2} \xi^{l+1} f(\xi)$ .... [15]

Substituting from equation (15) into equation (12) we have

$$\frac{d^2F}{d\xi^2} + 2\left[\frac{l+1}{\xi} - \xi\right]\frac{dF}{d\xi} + 2\left(\lambda - l - \frac{3}{2}\right)F = 0 \text{ .... [16]}$$

Let $F(\xi) = \sum a_k \xi^k$

Substituting into equation (16) we have

$$\sum_{k=k_0}^{\infty}\left[k(k-1)a_k\xi^{k-2}+2ka_k\left(\frac{l+1}{\xi}-\xi\right)\xi^{k-1}\right.$$

$$\left.+2\left(\lambda-l-\frac{3}{2}\right)a_k\xi^k\right]$$

Equating the coefficients of ξ^k in both sides we have

$$(k+2)(k+2l+3)a_{k+2}-\left(k+l+\frac{3}{2}-\lambda\right)a_k=0$$

If this series cut off at $k=p$ we find that

$$a_p\neq 0$$

$$\text{But}\quad a_{p+2}=0$$

Therefore

$$\left(p+l+\frac{3}{2}-\lambda\right)a_p=0$$

$$p+l+\frac{3}{2}-\lambda=0$$

$$\lambda=p+l+\frac{3}{2}$$

If the series begin with $k_0=0$, p must be even

Therefore

$$p=2n \quad n=0,1,2,\cdots$$

$$\therefore \lambda=2n+l+\frac{3}{2}\qquad\text{[17]}$$

From (11-a) and (17) we obtain the eigen energy as:

$$E_n = \hbar\omega\lambda = \hbar\omega\left(2n + l + \frac{3}{2}\right) \qquad [18]$$

The radial function

$$f_n(r) = \frac{U}{r} = \frac{U}{\xi\left(\frac{\hbar}{\mu\omega}\right)^{1/2}} = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} \xi^{-1} U$$

$$f_n(r) = \left(\frac{\mu\omega}{\hbar}\right)^{1/2} \xi^l e^{-\frac{1}{2}\xi^2} F_n(\xi) \qquad [19]$$

and the eigen function corresponding to the eigenenergy (18) can be given from (7,8,19) as follow:

$$\Psi_{nlm}(r,\theta,\varphi) = c f(r) f(\theta) f(\varphi)$$

$$= c\xi^l e^{-\frac{1}{2}\xi^2} F_n(\xi) P_{lm}(\cos\theta) e^{im\varphi}$$

Where $m = 0, \pm 1, \pm 2, \cdots, \pm l$

Problems

1- Show that

$$[L_x, L_y] = i\hbar L_z \;,[L_y, L_z] = i\hbar L_x \;,[L_z, L_x] = i\hbar L_y$$

$$[L^2, L_x] = [L^2, L_y] = [L^2, L_z] = 0$$

2- Show that

$$[\hat{L}_\alpha, \alpha] = 0 \quad ,[\hat{L}_\alpha, \beta] = -\frac{\hbar}{i}\gamma$$

3- Show that

$$[\hat{L}_\alpha, \hat{P}_\alpha] = 0 \quad ,[\hat{L}_\alpha, \hat{P}_\beta] = i\hbar \hat{P}_\gamma$$

4- Prove that

$$L_+ = L_x + iL_y = -i\hbar\left[i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}\right]e^{i\varphi}$$

$$= -i\hbar\left[-i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}\right]e^{-i\varphi}$$

5- For the one dimensional hormone oscillator, find the normal equation constant of the wave function

6- The potential energy of a three-dimensional harmonic oscillator is given by:

$$V = \frac{1}{2}\mu\left(\omega_1^2 x^2 + \omega_2^2 y^2 + \omega_3^2 z^2\right)$$

Solve the Schrödiger equation in Cartesian coordinates and obtain the energy levels and the corresponding normzlized wave function.

Show that for an isotropic oscillator ($\omega_1 = \omega_2 = \omega_3 = \omega$) the energy levels will be:

$$E_n = \left(N + \frac{3}{2}\right)\hbar\omega \quad ; \quad N = 0, 1, 2, \ldots$$

7- Prove that:

$$\psi = A \exp\left(\frac{-x^2}{4\langle x^2 \rangle}\right)$$

8- At time t = 0 the state of a free particle is specified by a wave function:

$$\psi(x,0) = A \exp\left(\frac{-x^2}{a^2} + ik_o x\right)$$

(i) Find the constant.

(ii) Calculate the expectation values of x and P.

9- For the one dimensional harmonic oscillator prove that:

$$\langle x^2 \rangle = \left(\frac{\hbar}{m\omega}\right)^{3/2}\left(n + \frac{1}{2}\right)$$

10- Prove that:

$$L + Y_l^m = \hbar\sqrt{(l-m)(l+m+1)}Y_l^{m+1}$$

$$L - Y_l^m = \hbar\sqrt{(l+m)(l-m+1)}Y_l^{m+1}$$

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